

Preparation and properties of colorless and transparent alicyclic polyimide composite films with organophosphate flame retardant

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Abstract: Various endeavors on improving the flame retardant properties of the alicyclic colorless and transparent polyimide (PI) film derived from 1,2,4,5-cyclohexane-tetracarboxylic dianhydride (CHDA) and 4,4'-oxydianiline (ODA) have been performed. For this purpose, several organic flame retardants (FRs), including organophosphate type FR (FR-1), organosilicone type FR (FR-2) and organic bromo-resin type FR (FR-3) were combined with the pristine CHDA-ODA films aiming at improving its flame retardancy while maintaining the intrinsic thermal stability and optical transparency. Experimental results indicated that only FR-1 could successfully achieve the good combined thermal, optical and flame retardancy characteristics for the derived PI composite films when its loading amount was below 10 wt% in the composite films. For instance, PI composite film containing 5wt% FR-1 (PI-2) showed an UL-94 VTM-0 class of flame retardancy, a 5% weight loss temperature ($T_{5\%}$) of 404°C, a glass transition temperature (T_g) of 325.6°C, and a transmittance of 86.4% at the wavelength of 450 nm, respectively. These thermal and optical data were all comparable to those of the pristine PI(CHDA-ODA) film. Further increasing of the FR-1 loading in the composite films led to apparent deterioration of the optical transparency for the films.

Keywords: alicyclic polyimide; films; flame retardant; organophosphates; optical properties

1 INTRODUCTION

Polyimides (PIs) have been widely used in aerospace, microelectronics, optoelectronics and other high-tech areas for more than half a century due to their excellent thermal, mechanical, and dielectric properties^[1-3]. Fully aromatic PIs are well-known as one of the most important heat-resistant polymers^[4]. However, wholly aromatic PIs are usually difficult to be processed due to their insoluble and infusible nature. Besides, most of aromatic PI films usually show colors from deep brown to yellow due to the formation of charge-transfer complexes (CTCs) between the diamine moiety and the dianhydride unit where the former acts as an electron donor and the latter as an electron acceptor [5]. The deep colors greatly limit the wide application of wholly aromatic PI films in flexible display substrate, transparent flexible copper clad laminate (FCCL) for optical integrated circuit, flexible solar cell, and other optical fields. In the past decades, extensive research and development of colorless and transparent PI films have been performed and the results showed that colorless of PI films can usually be achieved by introduction of alicyclic groups, fluorine-containing groups or asymmetric groups via prohibiting or reducing the formation of CTCs. However, the currently developed colorless and transparent PI films usually show a strong constraining relationship among their transparency, thermal and dimensional stability and flame retardancy. When the color and transparency of the PI films are improved, their intrinsic merits, including high thermal stability and good flame retardancy might be lost at the same time, especially for alicyclic type PI films.

Although the alicyclic groups can usually impart colorless and transparent features for the PI films, it also causes the deterioration of thermal and combustion properties for the derived PI films. In the literature, flame retardancy of PI films can either be improved by using flame retardant monomers, such as phosphine oxide containing diamines^[6] or using inorganic flame retardants (FRs). Studies have been reported that conventional inorganic FR fillers, including Al₂O₃^[7], clay^[8], silica^[9], titania^[10], aluminum nitride^[11] and

carbon nanotubes [12] have ever been incorporated into PI films in order to enhance the flame retardant performance of PI films. However, these inorganic FR fillers always tend to greatly reduce the light transmittance of derived PI composite films. Thus, organic FRs might be the optimal choice for the flame retardancy modification of alicyclic PI films.

Therefore, in the current work, as one of continuous work developing high performance PI films for high-tech applications, the endeavors for improving the flame retardancy of the colorless and transparent alicyclic PI films while maintaining their intrinsic thermal and optical properties were performed. For this purpose, several organic FRs, including organophosphate type (FR-1), organo- silicone type (FR-2) and organic bromo- resin type (FR-3) were combined with the pristine alicyclic PI film derived from the alicyclic 1,2,4,5-cyclohexanetetracarboxylic acid dianhydride (CHDA) and 4,4'-oxydianiline (ODA). The CHDA-ODA type of PI film is well-known for excellent optical transparency in the ultraviolet and visible light region and good mechanical properties; however it usually suffers from poor flame retardancy. The effects of incorporation of the organic FRs on the flame retardancy, thermal stability and optical properties of the PI composite films were investigated in detail.

2 EXPERIMENTAL

2.1 Material

1,2,4,5-Cyclohexanetetracarboxylic acid dianhydride (CHDA) was purchased from Weihai NewEra K&S New Material Co., Ltd., China and dried in vacuo at 180 °C for 12h prior to use. Polymerization grade 4,4'-oxydianiline (ODA) was purchased from Shandong Guansen Polymers Materials Science and Technology Inc., China and used as received. *N*-methyl-2-pyrrolidinone (NMP), γ -butyrolactone (GBL), and *N,N*-dimethylacetamide (DMAc) were purchased from Sigma-Aldrich and purified by distillation prior to use. Organophosphate type FR (FR-1) was synthesized in our laboratory. Organosilicone type FR (FR-2) and organic bromo-resin type FR (FR-3) were kindly supplied by the customers. The other reagents were commercially available products and used without further purification.

2.2 Characterization

Molecular weights, including the number average molecular weight (M_n) and weight average molecular weight (M_w) of the PI resins were measured using a Shimadzu gel permeation chromatography (GPC) systems with a LC-20AD dual-plunger parallel-flow pumps (D1-LC), a SIL-20A is a total-volume injection-type autosampler, a CTO-20A column oven, and a RID-20A detector. HPLC grade NMP was used as the mobile phase at a flow rate of 1.0 mL/min. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum was obtained on a Bruker Tensor-27 FT-IR spectrometer. Wide-angle X-ray diffraction (WAXRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu-K α 1 radiation, operated at 40 kV and 200 mA. X-ray diffractometer with Cu-K α 1 radiation, operated at 40 kV and 200 mA. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i- XL electron spectrometer from VG Scientific using a 300W MgK α radiation. The base pressure was 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from the adventitious carbon. The thicknesses of the PI films were measured surface profilometry (DekTak-XT, Bruker Instruments, USA).

Ultraviolet-visible (UV-Vis) spectra were recorded on a Hitachi U-3210 spectro- photometer at room temperature. The cutoff wavelength was defined as the point where the transmittance was zero in the spectrum. Yellow index (YI) and haze values of the PI films were measured using an X-rite color i7 spectrophotometer with PI film samples at a thickness of 25 μ m. The color parameters were calculated according to a CIE Lab equation. L^* is the lightness, where 100 means white and 0 implies black. A positive a^* means a red color, and a negative one indicates a green color. A positive b^* means a yellow color, and a negative one indicates a blue color. Thermogravimetric analysis (TGA) was performed on a TA-Q50 thermal

analysis system at a heating rate of 10 °C/min in nitrogen. Differential scanning calorimetry (DSC) was carried on a TA-Q 100 thermal analysis system at a heating rate of 10 °C/min in nitrogen.

The flame retardancy of the PI films was measured using a UL-94 VTM (vertical thin film) test. In the test, a 20 cm×5 cm×0.02 mm sample was wrapped around a mandrel, and then the mandrel was removed. The two flame tests lasted for 3 s for the UL-94 measurements. After the first ignition, the flame was removed and the time for the film to self-extinguishing time (t_1) was recorded. Cotton ignition was noted if the polymer dripped during the test. After cooling, the second ignition was performed on the same sample and the self-extinguishing time (t_2) and dripping characteristics were recorded. If the sum of t_1 and t_2 was less than 10s without any dripping, the flame retardant rating of the polymer was considered as VTM-0. If the sum of t_1 and t_2 was in the range of 10-30 s without any dripping, the flame retardant rating of the polymer was considered as VTM-1.

2.3 Synthesis of polyimide resin

Into a 500 mL three-necked, round- bottomed flask equipped with a mechanical stirrer, a Dean-Stark trap and a nitrogen inlet, ODA (20.0240 g, 100 mmol) was dissolved in GBL (150 g) to afford a clear solution. Then, CHDA (22.4170 g, 100 mmol) was added in one batch and an additional volume of GBL (20 g) was added to wash the residual dianhydride. After stirring 30 min at room temperature, a pale-brown viscous solution was obtained and an exothermic reaction up to 60-70 °C was observed. Isoquinoline (0.5 g) and toluene (150 mL) was added as imidization catalyst and azeotropic agent, respectively. The reaction mixture was heated to 140 °C in nitrogen and maintained for 6h. During the reaction, the toluene-water azeotrope was distilled out of the system and collected in the Dean-Stark trap. Then, the reaction mixture was continuously heated to 180 °C and maintain for 3h. After cooling to room temperature, the viscous PI solution was carefully poured into an excess of ethanol to yield a silky white resin. The obtained white PI resin was collected and dried at 80 °C in vacuum for 24 h.

2.4 Preparation of polyimide films

PI resin prepared in Section 2.3 was dissolved in newly distilled DMAc and various amounts of FRs (5wt%, 10wt%, 15wt%, 20wt% and 25wt% based on the total solid) dissolved in DMAc were added. The solid content of the final composite solution was maintained at 20 wt%. Table 1 shows the detailed formulation of different FRs content used for the preparation of composite films. After the solution was mechanically mixed for 3h, the viscous PI composite solution was cast on clean and dust-free glass plates by a scraper, and then dried in a clean oven at 50°C (0.5h), 80°C (3h), 120°C (1h), 150°C (1h), 180°C (1h), 200°C (1h) and 260 °C (1h), respectively. The obtained PI composite films were peeled off in deionized water and then dried in a heated air circulation drying oven at 105°C for 4h.

Table 1 Formulation of PI samples filled with different amount of flame retardant

Sample codes	PI (g)	FR (g)	DMAc (g)	FR (wt%)
PI-1	10	0	40	0
PI-2	10	0.53	42.1	5
PI-3	10	1.11	44.4	10
PI-4	10	1.76	47.1	15
PI-5	10	2.50	50.0	20
PI-6	10	3.33	53.3	25

3 RESULTS AND DISCUSSION

3.1 Evaluation of FRs

In this study, a series of FR-containing PI composite films were prepared and characterized. In order to

achieve a balance among the desired properties of thermal, optical and combustion properties for the developed PI composite films, the characteristics of the tested three organic FRs were first evaluated. Figure 1 depicts the typical solubility test of the FR-1 in the good solvent DMAc for CHDA-ODA resin. A solubility as high as 20 wt% was achieved for all of the three FRs. This means that all of the three FRs might achieve a combination with the PI matrix at a molecular level.



Fig. 1 Solubility test of FR-1 in DMAc (20 wt%)

Secondly, the thermal stability of the FRs in air and nitrogen atmospheres were evaluated by TGA measurements and the plots were shown in Fig. 2. It can be clearly seen that, FR-3 with the bromo-substituted polymer structure exhibited the worst thermal stability with the 5% weight loss temperature ($T_{5\%}$) around 250 °C, which is the below the curing temperature of PI films (260°C). It means that FR-3 might decompose rapidly during the curing process of the PI film. Thus, it cannot be used for the flame retardancy improvement for the PI film. FR-1 and FR-2 exhibited a $T_{5\%}$ value of 365 °C and 481 °C, respectively. Thus, they could meet the thermal demands of the modification.

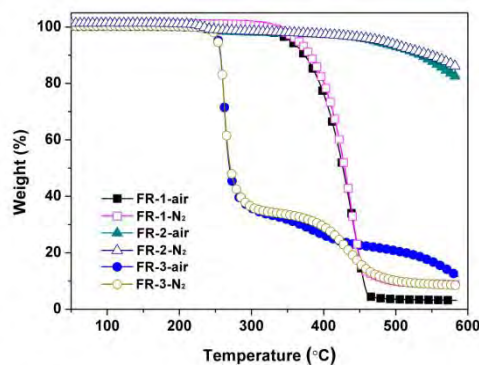


Fig. 2 Thermal stability of FRs in air and nitrogen atmospheres

Thirdly, the miscibility of the FR-1 and FR-2 with the PI film matrix was investigated. Figure 3 showed the appearance of the PI/FR-1 composite films on the logo of our university, CUGB. It can be obviously seen that PI-1~PI-3 with the FR-1 content of 0, 5 wt%, and 10 wt%, respectively, exhibited good optical transparency, indicating good miscibility of the FR filler and PI matrix. When the content of FR-1 was higher than 15 wt%, the film became opaque. For FR-2, the upper loading amount that keeping the films clear and transparent is about 5wt%.



Fig. 3 Appearance of PI/FR-1 composite films

On the whole, FR-1 possessed the best combined properties and thus was chosen for the further investigation.

3.2 PI synthesis and film preparation

Alicyclic PI resin was synthesized by a one-step high temperature polycondensation procedure from CHDA and ODA, as shown in Fig. 4. GBL (b.p. 204°C) was used as the reaction medium and the reaction system maintained homogeneous during the polymerization, indicating the good solubility of the PI in the solvent even at the imidized state.

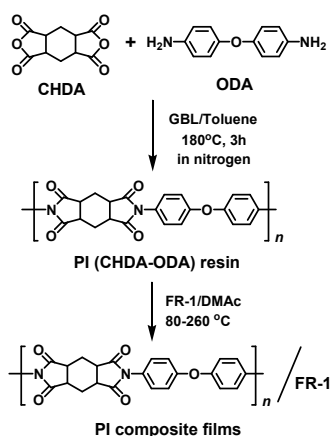


Fig. 4 Synthesis of PI resin and preparation of PI composite films

The M_n and M_w values of the PI resin were 154,189 g/mol and 269,262 g/mol, respectively. Thus, the polydispersity index (PDI) of the PI resin is about 1.75, indicating relatively narrow molecular weight distribution.

The PI resin was soluble in NMP, DMF, DMAc, GBL at a solid content of 15 wt% at room temperature. The obtained homogeneous PI solution showed good storage stability up to 1 year at room temperature. The FR-1 filler pre-dissolved in DMAc was successfully dispersed in the PI solution affording a composite solution with the FR-1 loading amount of 0-25 wt% in the total solid. Homogeneous and clear solution was obtained for all of the samples. After curing at temperatures up to 260 °C, PI-1~PI-6 composite films were obtained. Fig. 5 shows the ATR-FTIR spectra of FR-1 and the PI composite films. In the spectra, the characteristic absorptions attributed to the imide carbonyl located at 1777 cm^{-1} and 1704 cm^{-1} , and C-N at 1381 cm^{-1} were all clearly observed. This indicates that the PI film (CHDA-ODA) was successfully prepared. The intensity of peaks at 947 cm^{-1} assigned to the absorption of P-O-C in FR-1 increases gradually from PI-1 to PI-6. This means that flame retardant was successfully incorporated into the PI resin.

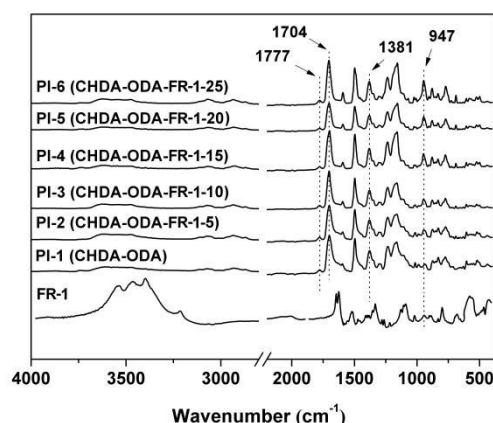


Fig. 5 ATR-FTIR spectra of FR-1 and PI composite films

The successful incorporation of FR-1 in the composite films can be further proven by the XPS measurements, as shown in Fig. 6. PI-1 showed the surface element composition of C1s, N1s, and O1s elements. However, PI-2~PI-6 showed an additional P2p absorption besides the C, N, and O elements. The

intensity of P2p absorption peaks increased with the increasing of the FR-1 loadings.

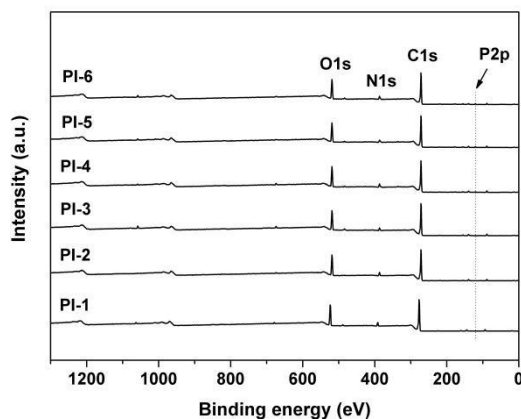


Fig. 6 XPS plots of PI composite films

At last, in order to analyze the composite films from a molecular level, the XRD analysis on FR-1 and the composite films were performed and the results are shown in Fig. 7. FR-1 exhibited crystalline nature with the diffraction angles in the range of 9.5-30°. The pristine CHDA-ODA film showed amorphous nature with weak peaks at the diffraction angle of about 17°. This indicates that introduction of the alicyclic structure destroyed the molecular regularity of the PI chains. For the PI composite films, PI-2 and PI-3 basically exhibited amorphous nature at a low level of FR-1 loading. However, a new peak around the diffraction angle of 9.5° gradually became stronger as the FR-1 loading increased. PI-4~PI-6 exhibited two peaks at 9.5° and 17°, respectively, indicating the existence of both of amorphous and crystalline regions in the polymers. This experimental results intimate that FR-1 might form aggregates when its loading amount was higher than 15wt%. The optical transparency of the PI-4~PI-6 composite films might deteriorate. This prediction is highly consistent with the appearance of PI composite films shown in Fig. 3, which will be quantitatively discussed below.

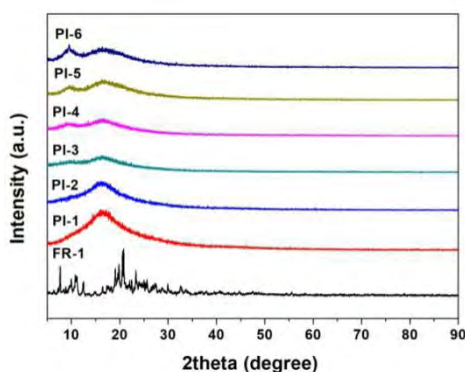


Fig. 7 XRD plots of FR-1 and PI films

In summary, PI/FR-1 composite films were successfully prepared in our work. The chemical structures of the composite films were confirmed and the FR-1 filler was successfully incorporated into the PI matrix.

3.3 Optical properties

The optical transparency of the PI composite films was quantitatively characterized by the UV-Vis and yellow index measurements and the optical data, including the cutoff wavelength (λ_{cutoff}), transmittance at 450 nm (T_{450}), yellow index (b^*), and haze were tabulated in Table 2. Figure 8 shows the UV-Vis spectra of PI/FR-1 and the PI/FR-2 films recorded in the range of wavelength from 200 to 800 nm.

It can be clearly seen that incorporation of FR filler didn't affect the λ_{cutoff} value of the composite films. For both of the systems, addition of the FR fillers at the low loading level slightly increased the transmittance

of the pristine PI films. For instance, PI-2 and PI-3 with a FR-1 loading of 5wt% and 10 wt% exhibited a T_{450} value of 86.4% and 87.0%, respectively, which was 5.3% and 5.9% higher than that of the pristine PI film (81.1%). This might be due to the fact that a small amount of FRs expanded the stacking density of PI molecular chains; thus facilitating the transmission of visible light. When the content of the FRs reaches a certain level, the FR molecules aggregated and hindered the transmission of visible light. This level is closely related with the miscibility of the FR fillers with the PI matrix. The upper limitation loading level might be 15 wt% for FR-1 and 5wt% for FR-2, as can be deduced from Fig. 8a and 8b, respectively.

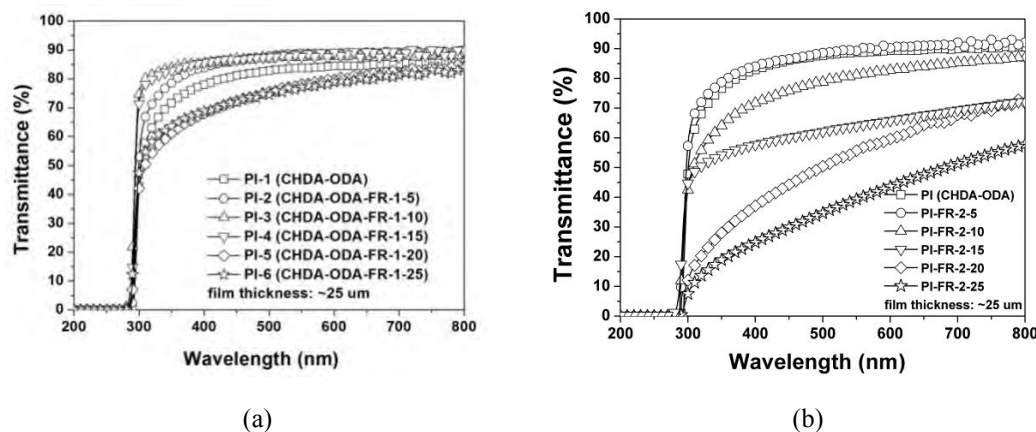


Fig. 8 UV-Vis curves PI composite films. (a) PI/FR-1; (b) PI/FR-2

With the increasing loading of FR-1, the optical transparency of the composite films rapidly deteriorated. PI-6 with the highest FR-1 loading showed a low T_{450} value of 72.5%. The deterioration of the optical properties of the PI composite films could be clearly reflected from the color parameters, including yellow indices and haze of the films. As can be seen from Fig. 3 that the yellow PI-6 film was nearly opaque, and the b^* and haze value was 10.94 and 83.44%, respectively. This value is much higher than that of the pristine PI film with the b^* and haze value of 1.21 and 1.79%, respectively. Nevertheless, PI-2 and PI-3 exhibited good balanced optical properties with high T_{450} and low color parameters.

3.4 Thermal properties

The influence of the incorporation of FR-1 on the thermal stability of the composite films was evaluated by TGA and DSC measurements and the data were shown in Table 2. Fig. 9 showed the TGA curves of the films, revealing the thermal degradation behavior of the PI composite films at elevated temperature in nitrogen atmosphere. All the PI films were thermally stable before 300 °C. After that, a two-stage decomposition behaviors were clearly observed for PI-2~PI-6. The first stage was considered to be the decomposition of FR-1, while the second one was thought to be the degradation of the PI resin. The 5% decomposition temperatures ($T_{5\%}$) of the films decreased according to the order of PI-1>PI-2>PI-3>PI-4>PI-5>PI-6, which is consistent with the increasing loading of FR-1 in the composite films. For example, PI-6 with the highest FR-1 loading showed a $T_{5\%}$ value of 351 °C, which is 78°C lower than that of pristine PI-1 film. The deterioration of the thermal stability of the PI composite films is mainly attributed to the inferior thermal stability of FR-1, which showing a $T_{5\%}$ value of 365 °C, as shown in Fig. 2. Although the PI composite films showed an inferior thermal decomposition temperature to the pristine PI film, the char yields of the composite films at 760°C (CY_{760} , 57.7-66.5%) were all higher than that of the pure PI film (37.6%). This is mainly due to the formation of inert and thermally stable phosphorus-containing phosphates at elevated temperatures for PI-2~PI-6 with organophosphate type FRs.

Glass transition temperatures (T_g) values were obtained from the DSC measurements, as shown in Fig. 10. All the composite films (PI-2~PI-6) exhibited a bit lower T_g values than that of the pure PI-2 ($T_g=346.8$ °C), indicating that incorporation of FR-1 slightly sacrificed the thermal stability of the PI films. This is mainly

attributed to the plasticizing effects of FR-1 in the system.

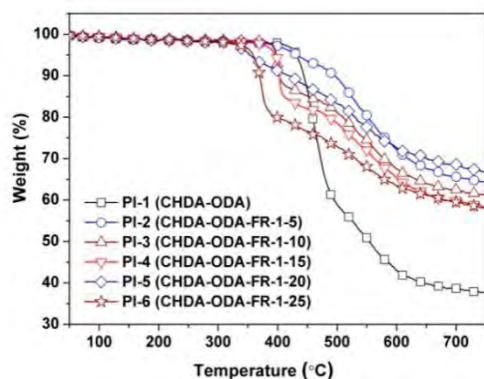


Fig. 9 TGA plots of PI composite films

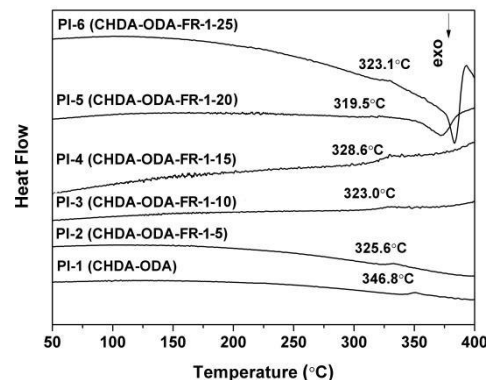


Fig. 10 DSC plots of PI composite films

Table 2 Thermal and optical properties of composite PIs.

Samples	λ (nm)	T_{450}^a (%)	YI	haze	T_g^b (°C)	$T_{5\%}^c$ (°C)	CY_{760}^d (%)
PI-1	288	81.1	1.21	1.79	346.8	429	37.6
PI-2	285	86.4	2.37	2.14	325.6	404	61.2
PI-3	281	87.0	5.49	2.23	323.0	397	58.9
PI-4	279	86.6	6.33	43.19	328.6	394	58.4
PI-5	281	72.5	10.65	68.17	319.5	356	66.5
PI-6	279	71.9	10.94	83.44	323.1	351	57.7

^a Transmittance of samples in 450 nm; ^b Measured by DSC at a heat rate of 10°C/min. ^c 5% decomposition temperature under a nitrogen atmosphere; ^d Char yield, residual weight percentage at 760°C under a nitrogen atmosphere.

3.5 Flame retardant properties

The flame retardant properties of the FR-1 combined PI films were studied in terms of the UL-94 VTM measurements. The combustion data of the PI composite films is summarized in Table 3. According to the UL-94 VTM text, the total burning time, that was the sum of t_1 and t_2 , was all less than 5s for the developed PI composite films with the FR-1 content of 5wt% (PI-2), and 10wt% (PI-3), respectively. The result indicated that both of the PI composite films achieved a level of VTM-0 flame retardancy. This is undoubtedly quite beneficial for their applications in some specific areas, such as automotive industry, electrical and electronic industry, construction industry, and other high-tech fields requiring the flame retardant standard for the materials.

Table 3 UL-94 VTM data of the PI composite films

samples	t_1 (s)	t_2 (s)	t_1+t_2 (s)	Dripping	UL-94 VTM
PI-2	1	0	1	no	VTM-0
PI-3	0	0	0	no	VTM-0

4 CONCLUSIONS

In the current work, the flame retardancy was successfully achieved for a standard colorless and transparent semi-alicyclic PI film derived from CHDA and ODA. A combustion level of UL 94 VTM-0 was achieved by combination of one organo- phosphate type FR with the loading amounts below 10 wt% with the CHDA-ODA matrix. The intrinsic thermal and optical characteristics of the pristine PI film were basically maintained. The colorless and transparent PI composite films with the desired high-temperature resistance, good optical transmittance, and excellent flame retardancy are expected to be applied as advanced

materials for automotive, microelectronic, optoelectronic and other high-tech areas.

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