Influence of Hydrogen-Bonding Interaction Introduced by Filled Oligomer on Bulk Properties of Blended Polyimide Films

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ABSTRACT: Specific structure oligomer is designed and synthesized to fill "blank interaction points" left among polyimide (PI) rigid-rod structure in order to further enhance the interaction between PI macromolecules. An oligomer, 4,4′-bisbenzamide diphenyl ether (BADE) containing amide groups as proton donor, was blended with polyamic acid (PAA) solution to modify PI of pyromellitic dianhydride and 4,4′-oxydianiline. Fourier transform infrared and dynamic mechanical analyses show that hydrogen-bonding interaction occurs between N—H groups and PI chains. This resulted interchain interaction increases the tensile strength of blended PI films from 115.9 to 135.6 MPa, about 17.0% improvement, with BADE content surprisingly up to 20 wt %. BADE is uniformly dispersed without aggregation within a saturated amount of 20 wt % through wide angle X-ray diffraction and morphology characterization. Moreover, rheological measurements indicate that the processability of PAA solution is maintained after introduction of BADE. The obtained PI films still have excellent thermal stability. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40498.

INTRODUCTION

Aromatic polyimides (PIs) have been recognized as one of the important members in the family of high-performance materials that can be used for a wide range of applications in fibers, films, coatings and composite matrices due to their excellent dielectric properties, outstanding thermal stability, good chemical and irradiation resistances.[1,2] However, the mechanical properties of the prepared PIs so far are not adequate enough to meet the requirement of the advanced composites. To meet the requirements for the advanced application in the severe environment, the mechanical properties of PIs need to be highly improved with little sacrifice of other excellent characteristics at the same time, which is still an urgent and challenging task of research.[3,4]

Currently, many methods have been employed to improve the mechanical properties of PIs. Among them, incorporation rigid aromatic heterocyclic units to increase the rigidity of the polymer backbone and introducing additional intermolecular associations such as hydrogen bonding and/or chemical crosslinking have been reported to be two of the most efficient approaches.[5,6] As we know, hydrogen bonding, as the strongest

physical interaction, is a useful way to improve the mechanical properties of materials, which is found in polyamide fibers and polyvinyl alcohol fibers, resulting in their high tensile strength and initial modulus.[7–9] This fact suggests that the introduction of strong hydrogen bonding into PI systems can improve the mechanical properties of PIs. However, PIs generally have no hydrogen bonding between the main chains because of the absence of proton donors after the imidization process, which may be the reason why the tensile strength of PI fibers is lower than that of polyamide fibers (e.g., Kevlar), poly[2,6-diimidazo(4,5-b: 4′,5′-e) pyridinylene-1,4(2,5-dihydroxy)phenylen] fiber, PIPD (called M5).[10]

Introduction of fillers containing hydrogen-bonding site donor and acceptor into PI system, which is capable of participating in specific interactions, has been widely investigated in recent years.[11–14] Yan Wang et al.[15] observed that the blends of Matrimid 5218 polyimide and polybenzimidazole with Torlon polyamide-imide were miscible at a molecular level over the whole composition range due to the existence of hydrogen-bonding interactions in these two polymer blend systems. Longbo Luo et al.[16] investigated that a novel diamine monomer,

Additional Supporting Information may be found in the online version of this article.
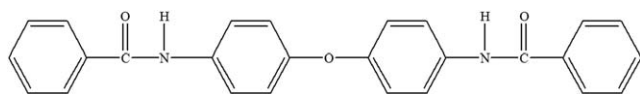
Figure 1. Chemical structure formula of BADE.

4-amino-N-(4-aminophenyl)-benzamide (DABA) containing amide group, was introduced into the PMDA-ODA polyimide, resulting in the improvement of mechanical properties due to formation of hydrogen bonding between the main chains. Hongqing Niu et al.[17,18] prepared a high-performance copolyimide (co-PI) fiber via a two-step polymerization/imidization process based on a new design of introducing an aromatic heterocyclic diamine monomer, 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone (AAQ) into rigid homopolyimide backbones of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and p-phenylenediamine (p-PDA). The AAQ was designed as the third monomer and copolymerized with the rigid BPDA and p-PDA system to enhance intermolecular interactions via hydrogen bonding and crosslinking. However, aromatic polyimides (PIs) are infusible and insoluble, so it cannot be reprocessed by solution or melting. Furthermore, dynamic viscosity of the PI precursor, polyamic acid (PAA) solution, is significantly increased after the introduction of hydrogen bonds into the backbone structures of PIs. It is urgent to find a way to improve the mechanical properties of aromatic PI while maintaining or improving the processing performance of precursor PAA solution, which has been a pursued research objective in the field of PI materials.

Because of its special molecular structure, PIs possess typical rigid-rod chain structure, which results in the decrease of molecular chain mobility and less conformation. Therefore, there are still "blank interaction points" and large free volume space left among macromolecular chains compared with flexible chain polymers. Inspired by these known successes above, specific structure oligomer can be used to blend with PAA solution to fill those "blank interaction points" to further enhance the interaction between PI macromolecules. In this study, a kind of oligomer, 4,4′-bisbenzamide diphenyl ether (BADE) containing amide groups as the proton donor shown in Figure 1, was designed and synthesized. The experiment results indicate that the incorporation of BADE could effectively fill those "blank interaction points" and form intermolecular hydrogen bonding with PI macromolecular chains, which results in the improve-

ment of the mechanical properties of PI with the content of BADE surprisingly up to 20 wt %. Simultaneously, plasticizing effect of BADE resulting from its low molecular weight and easy movement characteristic contributes to the processability of PAA solution.

EXPERIMENTAL

Materials

Benzoyl chloride (analytical grade) was provided by Chengdu Kelong Chemical Reagent (Chengdu, China). The 4,4′-oxydianiline (ODA) was obtained from Shanghai Synthetic Resin Research Institute and was recrystallized in ethanol prior to use. Pyromellitic dianhydride (PMDA) was supplied by Shanghai Synthetic Resin Research Institute and was purified by sublimation under reduced pressure before use. The 5-(6)-amino-2-(4-aminophenyl) benzimidazole (PABZ) was purchased from Changshu Sunlight Fine Chemical (Suzhou, China). N-methyl-2-pyrrolidone (NMP), obtained from Shanghai Qunli Chemical (Shanghai, China), was distilled over P_2O_5 under reduced pressure. The 4,4′-bisbenzamide diphenyl ether (BADE) containing amide groups was designed and synthesized in our laboratory (see Synthesis and Characterization of BADE in Supporting Information).

Preparation of the Blended PI Films

In this article, PI was synthesized by a two-step method, namely first the precursor PAA solution was synthesized, and then it was cured by thermal imidization to obtain PI film. Two kinds of PAA solutions were synthesized by dissolving ODA and PABZ (molar ratio:10/0 and 7/3) in NMP followed by the addition of equimolar amount of PMDA in a three-necked round flask equipped with a stirrer, nitrogen inlet-tube and outlet-tube. The reaction mixture was stirred at room temperature under nitrogen atmosphere for about 17 h to yield a 10% solid content PAA solution. Different amount of BADE solution with 10% solid content was blended with PAA solutions by mechanical stirring for about 4 h. Then the oligomer was uniformly dispersed, and finally homogeneous PAA-BADE solutions were obtained to prepare a series of blended PI films. The solid content of PAA-BADE solution for knife casting is controlled at 10%. Besides, the ratio of 7 : 3 for ODA : PABZ is reasonable and practicable for PMDA-ODA-PABZ system. In practice, for PMDA-ODA PI system, the dynamic viscosity of the PI
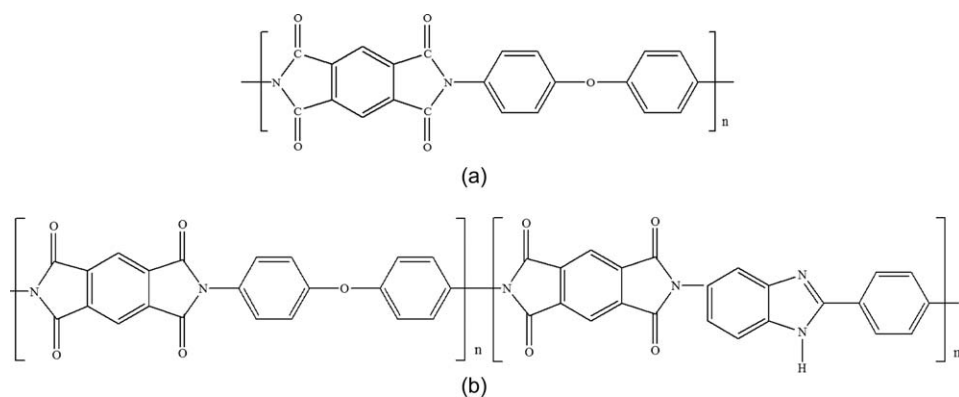

Figure 2. The main chain structures of (a) PIA (PMDA-ODA) system and (b) PIB (PMDA-ODA-PABZ) system.

Table I. Mechanical Properties of Blended PIA-BADE Films

Samples	Tensile strength (MPa)	Initial modulus (GPa)	Elongations (%)
PIA-BADE-0	115.9	1.50	32.2
PIA-BADE-5	123.8	1.53	39.9
PIA-BADE-8	127.6	1.63	41.3
PIA-BADE-10	130.7	1.80	42.9
PIA-BADE-15	132.7	1.83	43.2
PIA-BADE-20	135.6	1.87	44.4
PIA-BADE-30	103.3	2.42	5.5
PIA-BADE-40	82.3	3.77	3.5

precursor, polyamic acid (PAA) solution, is significantly increased after the introduction of PABZ into the backbone structures of PIs. The PAA solution can produce gel and can not be processed with the ratio of PABZ: ODA beyond 3 : 7.

The blended PI films were prepared by bulk thermal imidization. The PAA-BADE solutions were first cast onto clean and dry glass plates by a doctor's blade. The films were subsequently imidized by heating at 80°C for 2 h, 140°C for 2 h, 220°C for 2 h, and 320°C for 2 h in a vacuum oven. After the thermal treatment, the films were removed from the glass plates by immersing into water. Then the obtained PI films were further dried in a vacuum baking oven. The thickness of films ranges from 40 to 50 μm measured by thickness gauge. The two blended PI systems were denoted as PIA-BADE-X for PMDA-ODA system in Figure 2(a), PIB-BADE-X for PMDA-ODA-PABZ in Figure 2(b) (10 the mass content of BADE), such as PIA-BADE-10, PIB-BADE-10, etc. The —NH group in imidazole structure of PABZ in PMDA-ODA-PABZ system can form intermolecular hydrogen bonding between macromolecular chains. In contrast, there is no inherent hydrogen bonding interaction in the PMDA-ODA system.

Characterization

Mechanical properties, such as the initial modulus, tensile strength, and elongation at break, were measured on Instron Modle 5567 with a strain rate of 5 mm min^{-1} at ambient humidity and temperature. The specimens were 10 mm in width and 8 cm in length, and the fixture span was 20 mm.

Fourier transform infrared (FTIR) spectra of the blended PI films were measured on a Nicolet 560 infrared spectrometer in the range 4000–400 cm^{-1}. Dynamic mechanical analysis (DMA) behavior was performed on a TA Q800 instrument under N$_2$ atmosphere at a heating rate of 10°C min^{-1} in the range of 30–550°C, and the frequency applied was 1 Hz. Wide angle X-ray diffraction (WXRD) of blended PI films was carried out on a Philips X'Pert PRO-MPD instrument.

The morphological structure of the blended films was investigated using a DX-1 polarized light microscope (PLM) equipped with Nikon 500D SLR cameras at ambient temperature. To observe the morphology at higher magnifications, scanning electron microscopy (SEM) observation of the cross section was

performed with FEI Inspect F (FEI company, USA) under an accelerating voltage of 20 kV. The specimens were cry-fractured in liquid nitrogen, and the fractured sides were coated with gold prior to SEM observation.

The rheological property tests of PAA solution were conducted on TA-AR2000EX rheometer employing distribution-flow method at 25°C. The parallel plate geometry is 25 mm in diameter and shear rate (γ') is in range of 0.01–1000 s^{-1}. Thermal gravimetric analysis (TGA) was tested using TA Instrument TG-209F1 under N$_2$ atmosphere at a heating rate of 10°C min^{-1} in the range of 50–800°C.

RESULT AND DISCUSSION

Mechanical Properties

Mechanical properties of the blended PIA-BADE films are listed in Table I. The results of PIA-BADE-0 to PIA-BADE-20 show that the mechanical properties of the blended PIA-BADE films are significantly improved after the incorporation of BADE into PI systems, producing films with tensile strengths and initial modulus ranging from 115.9 MPa and 1.5GPa to 135.6 MPa and 1.87GPa, up to 17.0 and 24.7% improvement, respectively, compared with those of homo-PI PMDA-ODA film. Similar trend can be observed in breaking elongation, which is improved from 32.2 to 44.4%.

In the PIA-BADE system, BADE containing amide groups provides —N—H group, hence there is a strong tendency to form hydrogen bonding between BADE and macromolecular chains. The resulted hydrogen bonding contributes to forming physical crosslinking network, accounting for the improved mechanical properties. Meanwhile, due to its low molecular weight and easy movement characteristics BADE, to a certain extent, plays a plasticizing and lubricating action when the blended PI films are stretched, resulting in increase of the breaking elongation of the films. However, when the oligomer content of BADE exceeds 20 wt %, the tensile strength and elongation at break drop sharply.

To further investigate the filling effectiveness of BDAE for the PIs with different backbone structure, another PI system based on PMDA/ODA/PABZ with different amount of BADE (PIB-BADE) was prepared to make a comparison. PABZ, 5-(6)-amino-2-(4-aminophenyl) benzimidazole, is another diamine monomer containing the N—H group shown in Figure 3.

As shown in Table II, when the content of oligomer BADE reach 20 wt %, the tensile strength of PIB-BADE films increases from 147.1 MPa to 159.6 MPa, only about 8.5% improvement; similarly elongation at break ranges from 26.6 to 30.3%, about 13.8% improvement. The increase degree of tensile strength of PIB-BADE system is obviously lower than that of PIA-BADE films. Especially when BADE content ranges from 15 to 20 wt %, the tensile strength of PIB-BADE system increases from 158.3 to
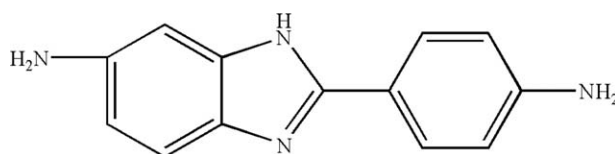
Figure 3. Chemical structure formula of PABZ.

Table II. Mechanical Properties of Blended PIB-BADE Films

Samples	Tensile strength (MPa)	Initial modulus (GPa)	Elongations (%)
PIB-BADE-0	147.1	2.24	26.6
PIB-BADE-5	149.7	2.15	27.0
PIB-BADE-8	152.2	2.08	28.4
PIB-BADE-10	155.2	2.05	28.5
PIB-BADE-15	158.3	2.15	29.4
PIB-BADE-20	159.6	2.01	30.3
PIB-BADE-30	133.8	2.14	11.5

159.6 MPa, the increase degree of which is less than that of PIA-BADE system ranging from 132.7 to 135.7 MPa.

It is because that the —NH group in imidazole structure of PABZ can form intermolecular inherent hydrogen bonding between macromolecular chains to occupy the "blank interaction points" left among macromolecular chains and shorten the interchain distance, resulting in less interaction points and free volume space left for BADE.[5] Therefore, the interaction between BADE and PI chains correspondingly reduces. The above results provide good evidence that oligomer indeed can effectively fill blank points in the PI system to improve mechanical properties, especially for PIA system with more blank interaction points and large free volume among macromolecular chains.

FTIR Characterization

To verify the existence of hydrogen-bonding interaction between these two components, FTIR was conducted to characterize the dependent band shift.[19,20] The FTIR results of blended PIA-BADE films are shown in Table III. The characteristic absorption bands of PI are observed at 1780 cm^{-1} (C=O of the cyclic imide symmetric stretching), 1720 cm^{-1} (C=O of the cyclic imide asymmetric stretching) and 1380 cm^{-1} (the C—N—C—stretching), respectively, indicating that the PIs were successfully prepared.[21]

Two new absorption bands at 3350 and 1660 cm^{-1} due to the —CONH— groups in BADE were identified in the FTIR spectra of PIA-BADE-3 to PIA-BADE-20, whereas that of PIA-BADE-0 cannot be found, indicating the successful incorporation of BADE into the PI system. The shape of N—H band becomes broader, and the stretching band of N—H obviously shifts to

**Table III.** The Peaks in FTIR Spectra of Blended PIA Films

|	$v_{N—H}$ (cm^{-1})	$v_{as\ C=O}$ (cm^{-1})	Amide (cm^{-1})
PIA-BADE-0	–	1725.06	–
PIA-BADE-3	3364.24	1723.62	1668.12
PIA-BADE-5	3362.68	1722.16	1666.88
PIA-BADE-8	3359.66	1719.87	1666.32
PIA-BADE-10	3358.73	1719.01	1664.46
PIA-BADE-15	3346.05	1718.35	1663.02
PIA-BADE-20	3344.32	1718.04	1662.21
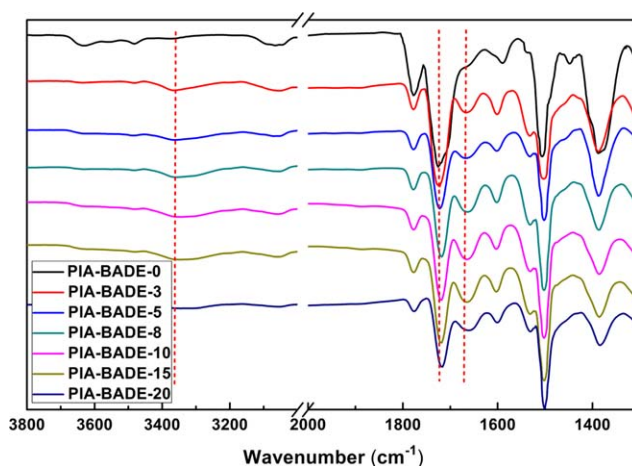
Figure 4. FTIR spectra of PIA-BADE films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lower wavenumbers with the increase of DABE content shown in Figure 4.[22] The amide C=O (amide I) stretching band at 1660 cm^{-1} and the v_s C=O at 1720 cm^{-1} similarly shift to low wavenumbers. The frequency shifts of the bands are 19.92, 5.91, and 7.02 cm^{-1} shown in Table III, corresponding to N—H group, amide carbonyls and imide carbonyls, respectively. The band location shift indicates that hydrogen-bonding interactions have truly occurred.

From the above results of FTIR, we can confirm that hydrogen bonding occurs between the N—H group and the C=O group of imide ring in Figure 5. Because of the existence of hydrogen bonding as strong intermolecular interaction, the tensile strength and initial modulus are significantly improved.

However, PIB system macromolecular chain structure containing —NH group can form intermolecular inherent hydrogen bonding compared with PIA system. The infrared spectra of the PIB with different content of BADE are presented in Figure 6. The absorption band at 3400 cm^{-1} is attributed to —NH group in imidazole structure of PABZ and amide group of BADE. The shifts of absorption bands in PIB-BADE system are listed in Table IV. As the content of oligomer BADE is increased, the N—H and C=O absorption bands of amide obviously shift to low wavenumbers. However, the C=O absorption band of imide ring slightly moves to higher wavenumber due to the break of inherent hydrogen bonding of PIB films. The frequency
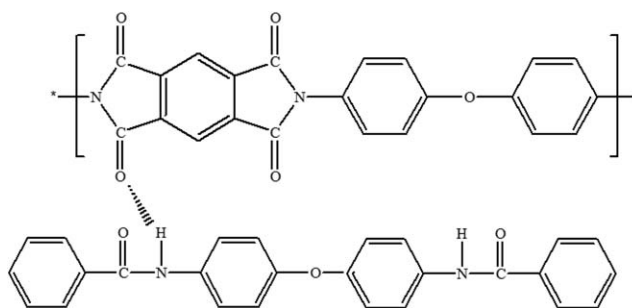
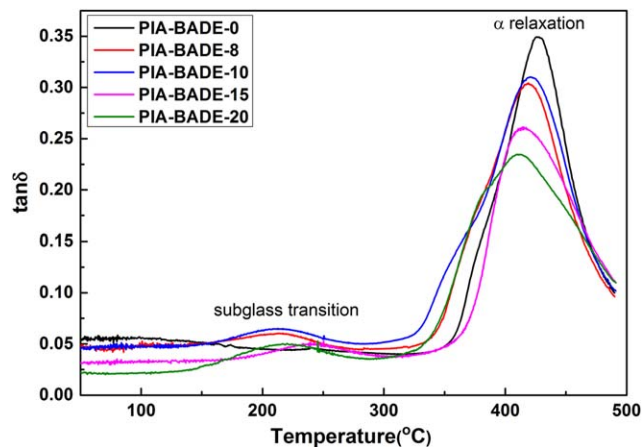**Figure 5.** The intermolecular hydrogen bond schematic between BADE and PI chains.
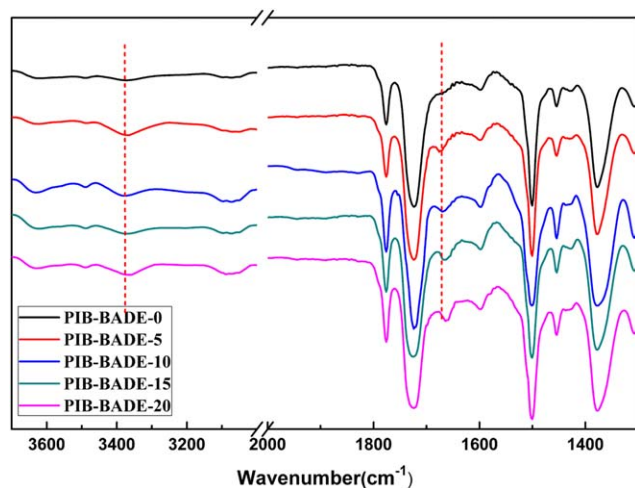
Figure 6. FTIR spectra of PIB-BADE films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shifts of the —NH and C=O absorption bands for PIB-BADE-0 to PIB-BADE-20 are 4.83 and 5.74 cm^{-1}, respectively, which shows that intermolecular hydrogen bonding interaction occurs between macromolecular chain and oligomer BADE.

The shift wavenumber of N—H and amide C=O absorption bands in PIB-BADE system is significantly lower than that of PIA-BADE system with the content of oligomer BADE up to 20 wt %. The hydrogen bonds form between intermacromolecular chains due to the introduction of PABZ containing —NH group into chain structure, which occupies hydrogen-bonding interaction sites among PI system. Therefore, hydrogen bonds forming between BADE and macromolecular chains obviously reduce, which is consistent with the result of mechanical properties.[23,24]

DMA Characterization

To further prove the existence of strong intermolecular interaction after addition of oligomer, DMA measurement was performed. Figure 7 shows the DMA curves for the homo-PI and blended films with different oligomer content. Two relaxation processes can be identified above room temperature. The one appearing at high temperature is the α relaxation which corresponds to the glass transition of the PI segments. As can be seen from Figure 7, tan δ value (α relaxation) of blended films decreases gradually from 0.32 to 0.25 with the increase in BADE content. It is well known that the low tan δ indicates hard chain segments motion, because it needs to overcome

Table IV. The Peaks in FTIR Spectra of Blended PIB Films

Samples	v N—H (cm^{-1})	v_{as} C=O (cm^{-1})	Amide (cm^{-1})
PIB-BADE-0	3373.66	1723.60	–
PIB-BADE-5	3372.64	1723.84	1672.68
PIB-BADE-10	3371.96	1723.93	1670.21
PIB-BADE-15	3370.74	1724.53	1668.31
PIB-BADE-20	3368.83	1725.18	1666.94

Figure 7. DMA curves of PIA-BADE films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

high friction. This high friction is caused by strong intermolecular interaction. Thus the decrease of the tan δ peak values indicates that the intermolecular interaction in PIA system
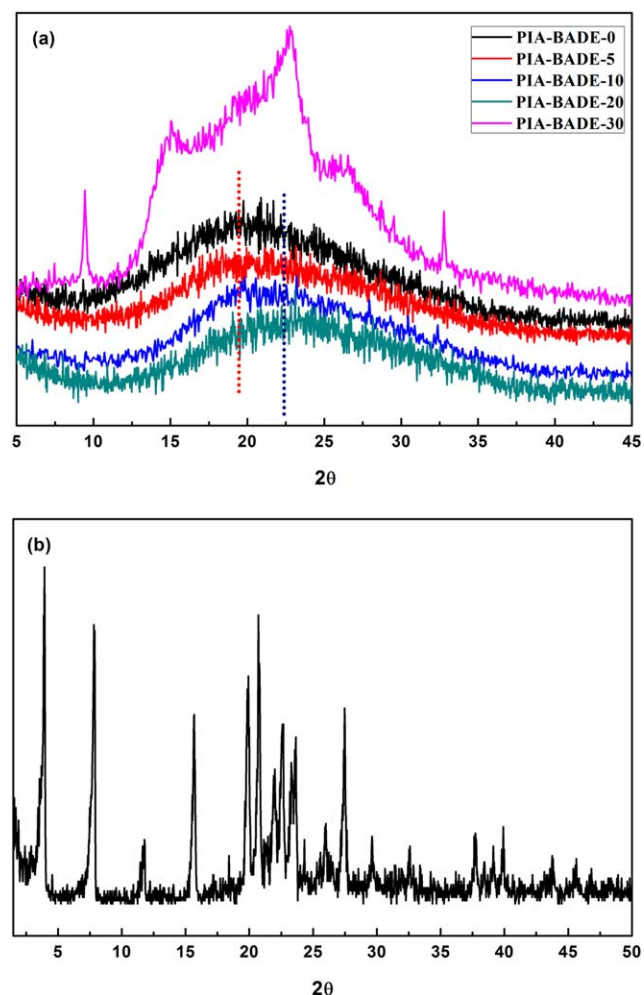
Figure 8. X-ray diffraction patterns of (a) PIA-BADE films and (b) oligomer BADE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Average Intermolecular Distance of PIA-BADE Films

Samples	2θ (°)	d-Space (Å)
PIA-BADE-0	19.9	4.64
PIA-BADE-5	20.1	4.40
PIA-BADE-10	20.5	4.33
PIA-BADE-20	22.1	4.01

increases when BADE containing amide groups was introduced into the PMDA/ODA system.[5,16]

In addition, another transition locating at relatively low temperature is referred to a subglass transition ranging from 200 to 220°C. Morphology characterization including PLM and SEM in the following discussion demonstrates that there is no aggregation and macroscopic phase separation for the blended PI films within a saturated amount of BADE (20%). Therefore, the transition at 200–220°C may be resulted from β relaxations or micro-phase separation.[25,26]

XRD and Morphology Characterization

The aggregation structure of the blended PIA-BADE films has an important impact on their performances, which was characterized by XRD. As shown in Figure 8(a), the XRD curves of the blended PIA-BADE films exhibit a broad amorphous halo at about 20° for PIA-BADE-0 to PIA-BADE-20. There is no characteristic crystallization peak. However, the virgin BADE has a very high crystallinity degree due to its low molecular weight and high regular structure shown in Figure 8(b). When the oligomer content increases to 30 wt %, the WAXD curve changes significantly shown in Figure 8(a) for PIA-BADE-30, similar to XRD curve of BADE. It can be concluded that there is no aggregation and macroscopic phase separation within a saturated amount of BADE (20%), which reveals that the distribution of BADE phase was homogeneous over the blended films. However, when the content of oligomer is up to 30%, there exists an obvious aggregation of oligomers, which is consistent with SEM and PLM results and accounts for the poor mechanical properties of PIA-BADE beyond 20 wt %.
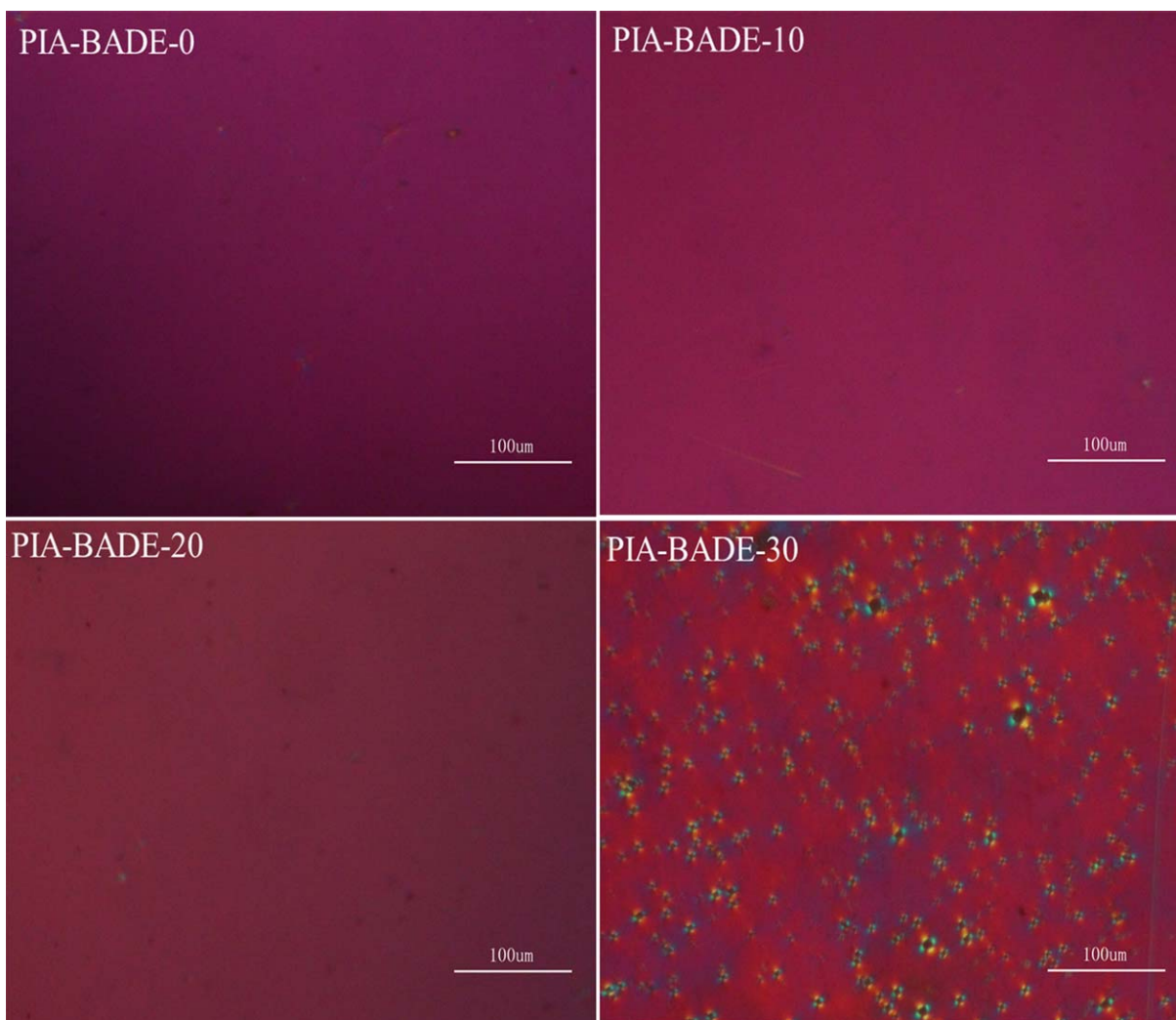
Figure 9. PLM images of the PIA-BADE-0, PIA-BADE-10, PIA-BADE-20, and PIA-BADE-30 blended films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
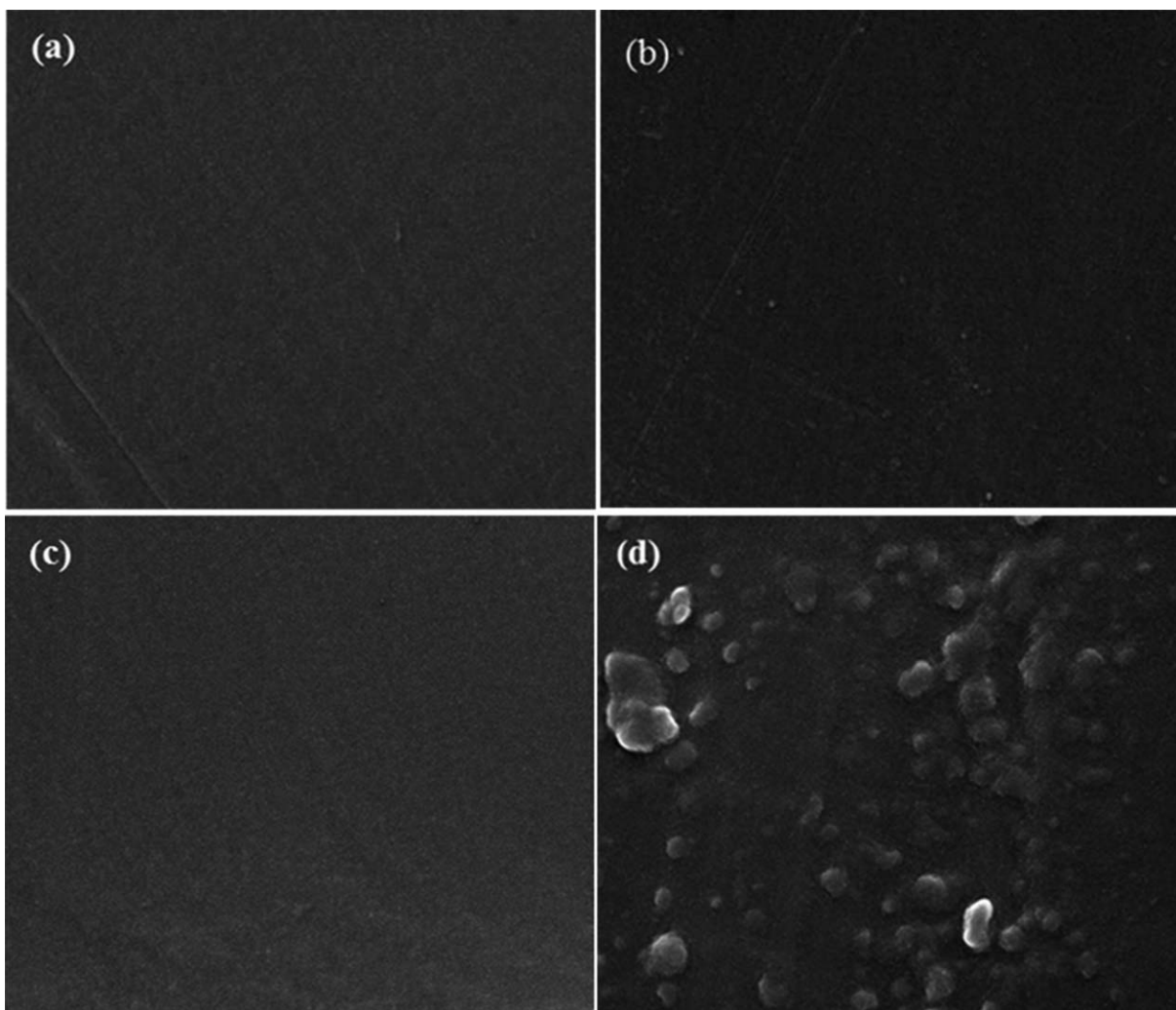
Figure 10. SEM micrographs of PIA-BADE films: (a) PIA-BADE-0; (b) PIA-BADE-10; (c) PIA-BADE-20; and (d) PIA-BADE-30.

Meanwhile, it can be observed that the amorphous halo position at about 20° shifts to higher shown in Figure 8(a), as the oligomer content increases from 0 to 20 wt %. The broad peak center on each X-ray pattern is attributed to the average inter-segmental distance (*d*-space) of polymer chains. The *d*-space can be calculated by substituting the scattering angles (2*θ*) of the peak into the Bragg's eq. (1). This method refers to the related literatures.[27–29]

$$2d \sin \theta = n\lambda \qquad (1)$$

where 2*θ* is the X-ray diffraction angle and *λ* is the wavelength of X-rays.

As shown in Table V, the peak of the virgin PI (PIA-BADE-0) film at 19.9° is the amorphous halo, giving a *d*-space of 4.64 Å, which corresponds to the average space of macromolecular chains. The average space of macromolecular chains of PIA-BADE-5 to PIA-BADE-20 gradually decreases from 4.64 Å to 4.01 Å with the increase in content of BADE. A smaller d-space means a tighter chain packing. Because of the introduction of oligomer, the hydrogen bonding interaction occurring between the carbonyl group of PIA and the —NH group of BADE makes a more dense arrangement of macromolecular chains, leading to a tighter structure.

The miscibility of the PIA-BADE blends was also studied through optical inspection using PLM at ambient temperature shown in Figure 9. It is clearly visible that the blend morphology for PIA-BADE-0 to PIA-BADE-20 is fairly clear and homogeneous. In contrast, there are many obvious crystalline bright specks in the specimen of the PIA-BADE-30, indicating that small molecules aggregate and precipitate from the PI matrix.

Figure 10 presents the SEM morphology photographs with magnification of 80,000×. As the content of BADE is gradually up to 20 wt %, the cross section of the films is compact and smooth shown in Figure 10(a–c), which indicates that the BADE obtains good dispersibility in blended PIA-BADE films. When the addition amount reaches 30 wt %, there are many obvious granular objects in cross section shown in Figure 10(d), and the aggregation of oligomers is obvious, which is consistent with the mechanical properties, XRD and PLM test results.
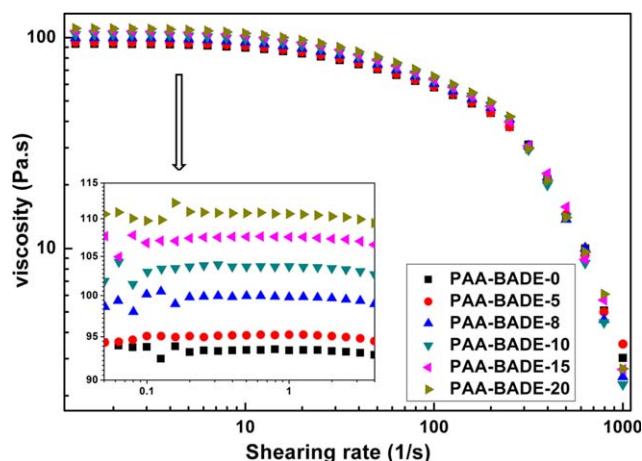
Figure 11. Relationship between viscosity (η) and shearing (γ') of PAA-BADE solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Rheological Properties

The contradiction between high performance and good processability of PIs has been the focus of scientific research. Rheological properties of the PAA solutions based on PMDA/ODA were measured by a parallel plate rheometer in Figure 11. The influence of the introduction of different content BADE on processability of the PAA solution has been investigated.

When BADE is introduced into the PAA solution, there exist two opposite effects as following: plasticizing effect induced by low molecular weight oligomer BADE; intermolecular hydrogen bonding interaction forming between PAA chains and oligomer. Under shearing interaction, macromolecular long-chain begins to deviate from the equilibrium conformation and orients along the flowing direction, and the formation and break of hydrogen bonding between molecular chains is dynamically reversible.

In the low shear rate region, although the physical crosslinking network induced by hydrogen bonds is damaged by shearing, it still has enough time to be reconstructed. The effect of intermolecular hydrogen bonding is dominant with respect to plasticizing effect. Therefore, as the BADE increases to 20 wt %, the zero shear viscosity (η_0) of PAA-BADE systems increases from 93.5 to 111.1 Pa s^{-1} in Table VI. When the shear rate increases to about 300 s^{-1}, the shear viscosity of PIA-BADE-0 to PIA-

Table VI. The Zero Shear Viscosity (η_0) and Viscosity (η) at 100 and 300 s^{-1} of PAA-BADE Solutions

Samples	Zero shear viscosity (η_0 Pa s^{-1})	Shear viscosity (100 s^{-1})	Shear viscosity (300 s^{-1})
PAA-BADE-0	93.5	58.0	31.2
PAA-BADE-5	96.7	58.6	29.8
PAA-BADE-8	99.9	60.5	30.5
PAA-BADE-10	103.7	62.6	29.3
PAA-BADE-15	107.4	63.2	30.2
PAA-BADE-20	111.1	65.4	29.7

Table VII. TGA Data of PIA-BADE Blended Polyimide Films

Samples	$T_{10\%}$ (°C)	T_{dmax} (°C)
PI-BADE-0	573.3	590.5
PI-BADE-8	575.4	592.5
PI-BADE-10	564.7	592.8
PI-BADE-15	570.1	591.8
PI-BADE-20	570.2	590.1

BADE-20 decreases from 31.2 to 29.7 Pa s^{-1}. It is because the damage of hydrogen bonding is more serious than reconstruction. The effect of intermolecular hydrogen bonding weakens, and plasticizing effect is dominant correspondingly (see Figure S4 in Supporting Information). From the above analyzed result, the introduction of BADE into polyimide system causes a little change in dynamic viscosity. Therefore, the processability of the PAA solution is almost maintained after introduction of BADE into PMDA-ODA system. Besides, there still has a slight improvement in processability at high shear region. When PAA solution is spun into fiber through the spinneret or processed into films, it is always under high shearing.

Thermal Properties

The thermal behavior of the blended PIA-BADE films was characterized by means of TGA. The results were tabulated in Table VII. Because of its special molecular structure, PI possesses excellent thermal properties.[30] As shown in Table VII, the blended PIs have a 10% weight loss temperature ($T_{10\%}$) in range of 564.7–575.4°C. Compared with that of homo-PMDA/ODA (PIA-BADE-0) films, the $T_{10\%}$ of the blended PI films slightly decreases. Besides, the maximum decomposition temperature (T_d) is still maintained at about 590°C (see Figure S5 in Supporting Information).

Additionally, regarding the temperature of tan δ peak in the DMA curves as T_g in Figure 7, the T_g of the PIA-BADE system shows a slight decreased trend, which ranges from 426 to 410°C for PIA-BADE-0 to PIA-BADE-20, only 3.85% reduction compared with that of the virgin PMDA/ODA (PIA-BADE-0). The heat resistance of PI is basically maintained after the addition of BADE. The thermal properties of the series of blended PIA-BADE films are still excellent.

CONCLUSION

The incorporation of BADE can effectively fill those "blank interaction points" and form intermolecular hydrogen bonding among PI macromolecular chains, which effectively strengthens the mechanical properties of PI with the content of BADE up to 20 wt %. BADE obtains good dispersibility without macroscopic phase separation within a saturated amount. Simultaneously, due to easy movement characteristic of small molecules, BADE can play a plasticizing and lubricating role, which contributes to processability of PAA solution. Therefore, the contradiction between high mechanical properties and processability of the polyimide material can be alleviated, to a certain extent, by adding specific structure small molecules. In addition, the thermal stability of blended PI films is still excellent. The results

in this article may provide a novel access to obtain high mechanical properties of PI materials while maintaining their processing properties.

ACKNOWLEDGMENTS

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