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Synthesis and properties of polyimide foams containing benzimidazole units

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In this research paper, a series of novel polyimide (PI) foams containing benzimidazole units were prepared derived from polyester ammonium salt (PEAS) precursor powders, which were synthesized by co-polymerization of benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA) with two diamines of 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and 4,4′-diaminodiphenyl ether (ODA) with various molar ratios. The effects of incorporation of BIA on the morphology, thermal and mechanical properties of co-polyimide (co-PI) foams were explored. The results show that the BIA has a significant influence on foaming degree of PEAS precursor powders. The density of co-polyimide foams increases with increasing the BIA content in the polymer chains. Moreover, the thermal stability of the resultant co-polyimide foams presents a remarkable upward trend with incorporating more BIA units into the polymer chains. As the BIA loading up to 30 mol%, the glass transition temperature of co-polyimide foams increases around 50 °C in comparison with the pristine polyimide foam. Furthermore, the compressive strength of the co-polyimide foams is in the range of 0.30–0.75 MPa, which is superior to their of commercial polyimide foams with the same density. The co-polyimide foams with higher thermal and mechanical properties expand their potential application in many high-tech fields such as aerospace and aviation industries.

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1. Introduction

Polyimide (PI) foams are a class of high-performance polymer materials and have been widely used in aerospace and aviation fields due to their excellent properties such as low weight, chemical stability, thermal insulating and acoustic absorbing.[1,2] However, the conventional polyimide foams are frequently challenged by weak mechanical properties, which limits its application in some load-bearing fields significantly. The mechanical properties of polyimide foams can be enhanced by increasing their density, however, lightweight is quite a valuable parameter for applications in weight-sensitive aerospace, transportation, or automobile industries. Therefore, it is of great significance to prepare lightweight polyimide foams with higher mechanical properties to satisfy structural material applications.

To overcome these problems, a lot of investigation has been concentrated on the design and preparation of novel polyimide foams with higher mechanical properties.[3–8] There are mainly two strategies improving the mechanical properties of polyimide foams by PEAS precursor powders foaming method. One strategy involving the introduction of inorganic fillers into the polymer matrix can enhance the mechanical properties of polyimide foams. Xu *et al.*[5] prepared aromatic polyimide/graphene foams through thermal foaming of poly(amic ester)/graphene oxide (GO) composite precursor powders. The research indicates that GOs act as heterogeneous nucleation sites in the foaming process, and the homogeneous dispersion of GOs within polymer matrix prefers to obtain foams with uniform cell size distributions. And the incorporation of GOs in the polymer matrix dramatically enhanced the flexural strength and compressive properties of the foam materials. Also, a novel polyimide/SiO_2 hybrid foams were successfully prepared by Qi *et al.*[6] The results revealed that the SiO_2 particles were well-dispersed in the polyimide matrix. The SiO_2 particles restricted the molecular mobility and enhanced their interfacial adhesion. The thermal stability, storage modulus, glass transition temperature, and dielectric constant of the hybrid foams were improved with the incorporation of SiO_2 particles. An alternative strategy is structural modification on the basis of the properties of polyimide materials mainly attributed to the structures of polymer chains. Wang *et al.*[7] prepared the rigid polyimide foams using *cis*-5-norbornene-2,3-dicarboxylic anhydride (NA) as end-capping agent. The cross-linked network was conformed in the thermal foaming process. The cross-linking points, molecular weight and density of polyimide foams can be controlled by adding different amount of NA, the mechanical could be improved from 0.1 MPa to 12.0 MPa by increasing the

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foam density from 50 kg m^{-3} to 420 kg m^{-3}. A series of rigid polyimide foams were prepared using poly(amic acid) (PAA) as foaming precursor by Zhan *et al.*[8] The cross-linking points and density of foams can be adjusted by controlling the content of isocyanate and water. The experiment indicates that the glass transition temperature of obtained polyimide foams increases markedly. Furthermore, the compressive strength also achieve a big growth up to 1.31 MPa at the density of 117.6 kg m^{-3}.

Recently, there are several methods reported in the literature for fabricating novel polyimide materials to improve its mechanical properties based on molecular design, such as combining the advantages of polybenzimidazoles (PBI) and polyimide to synthesize PBI–PI co-polymers to obtain the desired properties.[9–11] For example, the heterocyclic diamine 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) is an rigid asymmetric monomer, which has been successfully introduced into polyimide backbone in order to strengthen the mechanical and thermal properties of resulting materials in recent years.[12–14] Zhang's group have successfully synthesized a variety of polyimide materials such as fibers and films containing benzimidazole units,[15–17] and the results revealed that the mechanical and thermal properties of resultant materials improved significantly owing to the incorporation of benzimidazole units into the polyimide backbone. In order to adapt the specific environment, the mechanical and thermal properties of light-weight polyimide foams are still in need of further improvement. As we know, the incorporation of benzimidazole moieties into the polymer chains is one way to enhance the mechanical and thermal properties of polyimide materials. It may be also an effective approach to strengthen the mechanical and thermal properties of polyimide foams. However, the polyimide foams containing benzimidazole units have been rarely involved. Therefore, it is worthy to investigate the influence of benzimidazole units on the foaming process and properties of the resultant co-polyimide foams, which may serve as a general rule in designing and preparing novel polyimide foams.

The objective of this work is to fabricate light-weight aromatic co-polyimide foams with higher mechanical and thermal properties. The co-polyimide foams containing benzimidazole units were prepared *via* thermal foaming method derived from PEAS precursor powders, which was synthesized by co-polymerization of benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA) with two diamines of 2-(4-aminophenyl)-5-aminobenzimidazole (BIA) and 4,4′-diaminodiphenyl ether (ODA) with various molar ratios. In comparison, pristine polyimide (BTDA/ODA) foam also has been prepared. The effects of the incorporation of BIA moieties on foaming process of PEAS precursor powders and the physical properties of the resultant co-polyimide foams are systematically investigated.

2. Experimental

2.1 Materials

The benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA) was purchased from Shanghai Aladdin Industrial Co., Ltd, China (99% purity). 4,4′-Diaminodiphenyl ether (ODA) was obtained from Sinopharm Chemical Reagent Co., Ltd, China (99% purity). 2-(4-Aminophenyl)-5-aminobenzimidazole (BIA) was provided by Changzhou Sunlight Pharmaceutical Co., Ltd, China (98% purity). Ethanol and tetrahydrofuran (THF) were purchased from Guangzhou Chemical Reagent Co., Ltd, China. BTDA, ODA and BIA were dried at 120 °C in the vacuum oven for 12 hours prior to use. The THF was purified by distillation under reduced pressure over sodium prior to use. Other commercially available reagent grade chemicals were used without further purification.

2.2 Preparation of polyimide foams

PI-1 was prepared by the following procedures.[18,19] In a 250 mL round-bottom flask, BTDA (32.22 g, 0.1 mol) was first dispersed in a mixture solvent of ethanol (100 mL) and THF (20 mL) at room temperature under the protection of N_2 atmosphere. This solution was treated at 70 °C for 2 hours with magnetic stirring. A trace (3 drops) of 2-methylimidazole was added to accelerate the esterification reaction of BTDA. After the color of the solution changed from white to clear, the mixed monomers of ODA (0.09 mol, 18.02 g) and BIA (0.01 mol, 2.25 g) was added. The resulting mixture was stirred for 2 hours to yield a homogeneous precursor solution. The PEAS solution had a viscosity of 12.0 Pa s at room temperature and the solid content of the PEAS precursor solution was *ca.* 35 wt%. Secondly, the PEAS precursor solution was heated to remove the extra solvent by rotating distillation. The resultant resin was crushed into fine powders and separated into particles with diameters in the range of 75–100 μm by a group of sieves. Eventually, the PEAS precursor powders were treated for 3–5 hours at 80 °C until the weight remained unchanging and the residual solvent was maintained at 14 wt%.

The thermal foaming process was performed in a graphite mold. The mold was preheated at 80 °C for 1 h in oven. After being loaded with the precursor powders, the graphite mold was rapidly transferred into the heated oven. The foaming and imidization processes of the PEAS precursor powders were performed by the following schedule: 130 °C for 60 min, 200 °C for 120 min, 280 °C for 120 min. After this, the graphite mold was cooled down to room temperature.[20] The resultant co-polyimide foam was denoted as PI-1 and cut into the designed size dimensions for testing.

The same procedures used for PI-1 were repeated *via* adjusting the molar ratio of ODA/BIA (10 : 0, 8 : 2, 7 : 3 and 6 : 4) to fabricate other polyimide foams (Table 1). The resultant

Table 1 The properties of resultant PI and co-PI foams

PI	Cell diameter (μm)	Density (kg m^{-3})	Molar ratio (ODA/BIA)	Viscosity[a] (Pa s)
PI-0	615 ± 87	27	10 : 0	12.0
PI-1	440 ± 75	35	9 : 1	13.4
PI-2	339 ± 68	42	8 : 2	13.7
PI-3	220 ± 84	54	7 : 3	15.3

[a] The viscosity of the PEAS precursor solution, measured using digital rotational viscometer at room temperature.

polyimide foams were denoted as PI-0, PI-2, PI-3, PI-4 respectively. The overall process for the formation of co-polyimide foams is schematically described in Scheme 1.

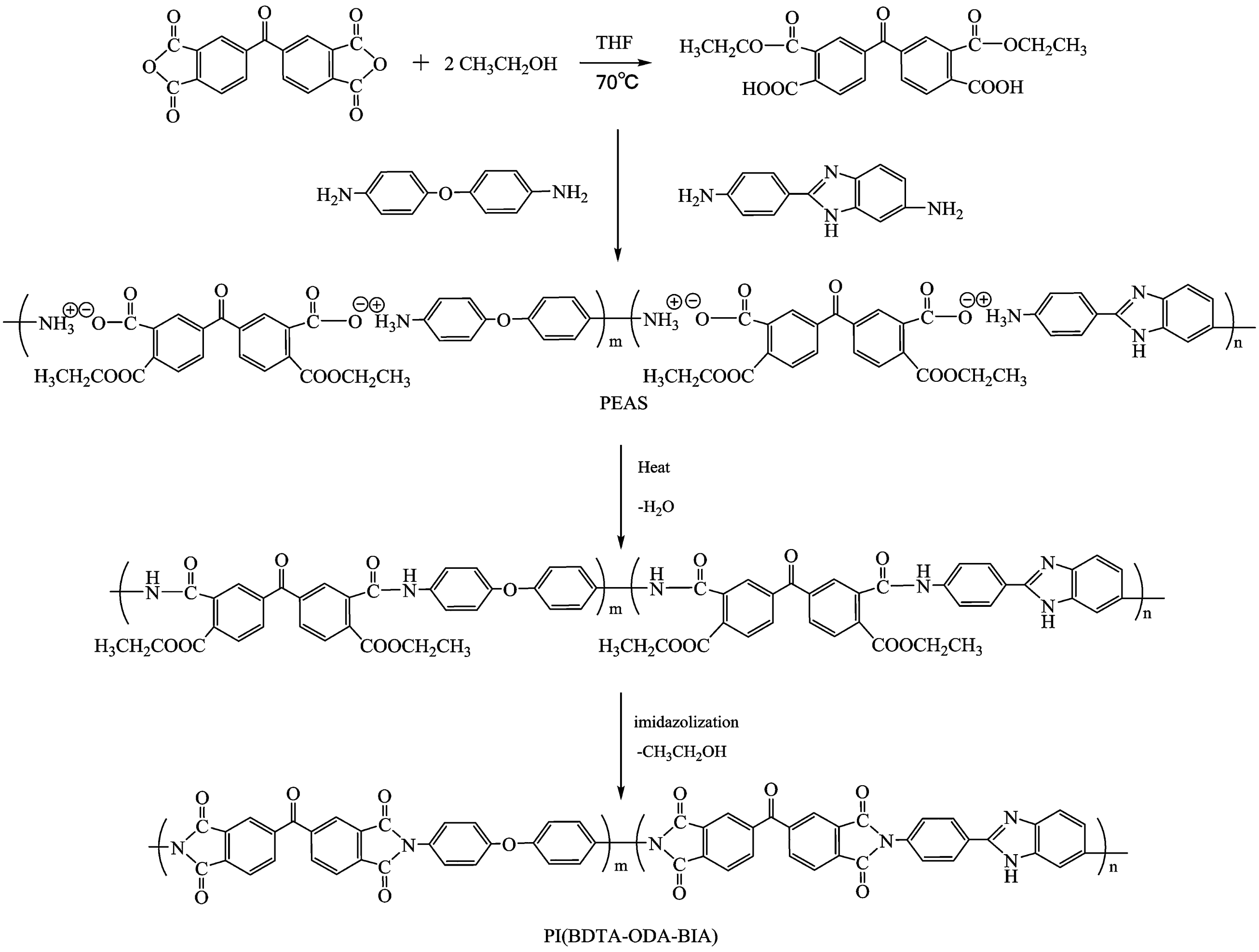
2.3 Characterization

The viscosity of the PEAS precursor solution was tested at room temperature using a digital rotational viscometer (CAP2000+L, Brookfield, USA) at a speed of 30 rpm. The chemical structures of polyimide foams were characterized on a Nicolet iS10 Fourier transform infrared spectrometer (FT-IR). The FT-IR measurements were performed in the 400–4000 cm^{-1} range by averaging 32 scans. Scanning electron microscope (SEM) images were obtained using a VEGA 3 electron microscope (TESCAN, Czech Republic). The calculation of cell diameter on the SEM photographs was conducted using software Image-Pro Plus. DSC (Mettler Toledo DSC_1) was used to study the glass transition temperature of the polyimide foams, the samples were heated from 25 °C to 370 °C at a ramp rate of 10 °C min^{-1} under the nitrogen atmosphere. Thermal gravimetric analysis (TGA) was performed on TGAQ 600 (TA Company) at a flow rate of 60 cm^3 min^{-1} under the nitrogen atmosphere. Sample tests were performed from 25 °C to 800 °C at a heating rate of 10 °C min^{-1}. Compressive properties of the foams were measured using a CMT 8502 multifunctional experimental machine at room temperature according to Chinese national standard GB/T8813. The compressive measurement were performed using specimens with a dimension of 50 mm × 50 mm × 25 mm (length, width and thickness) at a compressive rate of 3.0 mm min^{-1}, and the specimens were compressed to a total deflection of 80% of the full-part thickness.

3. Results and discussion

3.1 FT-IR analysis

The chemical structures of the resultant polyimide and co-polyimide foams with various ODA/BIA molar ratios were analyzed by FT-IR and the obtained results are shown in Fig. 1. The peaks at 1778 cm^{-1} and 1720 cm^{-1} are correspond to the C=O asymmetrical and symmetrical stretching of aromatic imide ring respectively. The peaks at 1380 cm^{-1} and 738 cm^{-1} represent the C–N stretching vibration and bending of imide ring.[21] The asymmetric and symmetric stretching of N–H bands in the benzimidazole could be observed in the regions of 3300–3400 cm^{-1} in three co-polyimide foams. The characteristic



Scheme 1 Synthesis of the co-PI (BTDA/ODA/BIA).

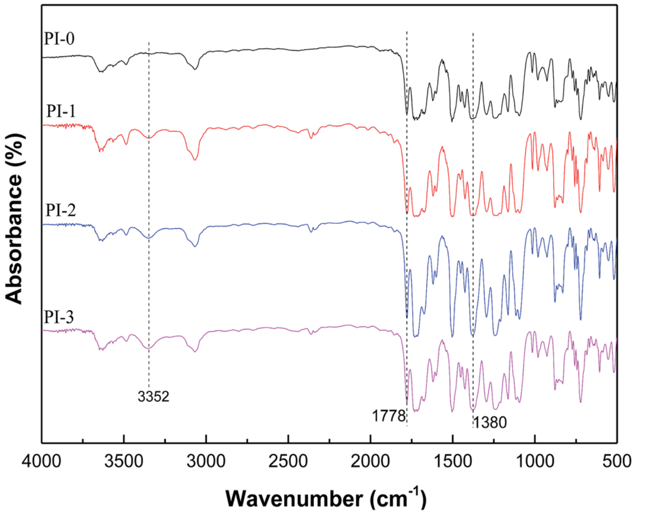


Fig. 1 The FT-IR spectra of the PI and co-PI foams.

peaks suggest the formation of imide ring and benzimidazole moieties have been successfully incorporated into the backbones of co-polyimide foams.[22]

3.2 The morphology of PI and co-PI foams

The scanning electron microscopy (SEM) was used to investigate the cell morphology of the resultant foams. The results are shown in Fig. 2. The average cell diameter has been statistically calculated from SEM images as displayed in Table 1. Drastic changes in the morphology can be observed from SEM after introduction of BIA into the polymer backbone. And the average cell diameter and foaming degree decreased with increasing the BIA content. However, the PEAS precursor powders could not be foamed partly or totally as the content of BIA exceeding 50 mol% at the same foaming temperature. These results indicate that the BIA content is a key factor controlling the density and foaming degree of PEAS precursor powders, and the high content of BIA is suitable for fabricating polyimide foams with high density.

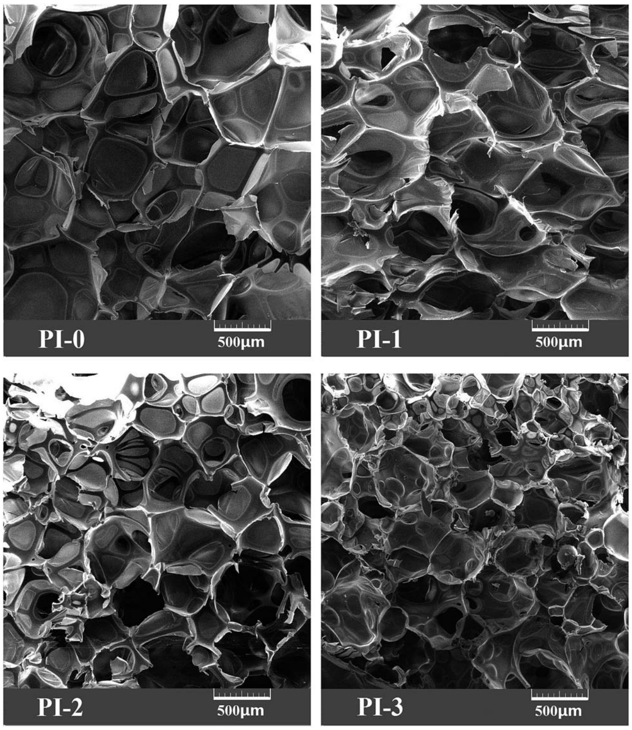


Fig. 2 SEM photographs of the PI and co-PI foams.

3.3 The foaming process of PEAS precursor powders

DSC technology was employed to trace the thermal foaming behavior of PEAS precursor powders under the heating conditions. Fig. 3 presented the DSC curves of PEAS precursor powders with different contents of BIA and the corresponding status of precursor powders at various temperatures. The foaming process can be divided into three steps as follows.[23] The first step was used to evaporate extra THF and ethanol (serving as foaming agents) within the solid PEAS precursor powders, which is critical in determining the foaming degree of PEAS precursor powders. Because excessive or insufficient residual solvent within PEAS precursor powders are not suitable for fabricating polyimide foams with uniform cell size distributions. The second step is foaming process, the PEAS precursor powders melted and inflated to microspheres under the given temperature during this process. The cell structures could be formed with a further growth of microspheres owing to the collision.[24] Following this, the imidization process endow polyimide foams with high flexible and mechanical properties. The polyimide foams with uniform morphology can be obtained by controlling these parameters that governs the powders inflation kinematics. In principle, the foaming process of PEAS precursor powders were mainly determined by the following four factors: chemical structure of PEAS, size of precursor particles, foaming temperature and content of residual solvent. In this study, the foaming temperature and the content of residual solvent were same, therefore, the

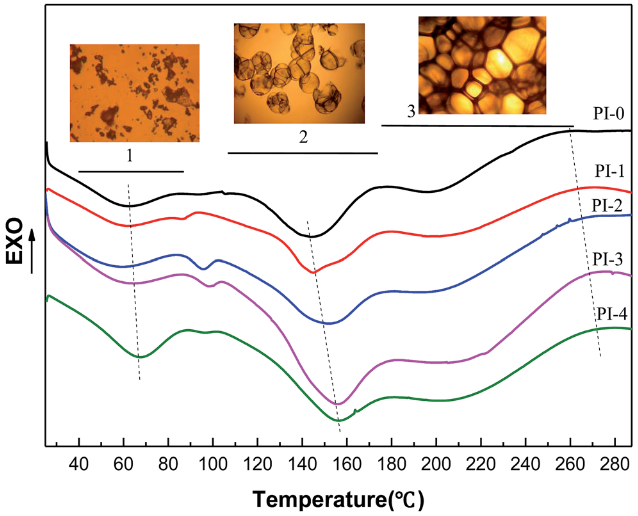


Fig. 3 DSC spectra of the PEAS precursor powders.

morphology of resultant co-polyimide foams were mainly determined by the chemical structure and the size of PEAS precursor particles.

The most important factor that affects the foaming process is the structure of PEAS precursor, because the glass transition temperature of PEAS precursor powders was mainly dominated by its structure. The previous experiments have revealed that the embedded nuclei are able to grow by diffusion and expansion of the volatile solvent agent within the particles when the temperature arrives to the corresponding glass transition temperature of the PEAS precursor. From Fig. 3 it can be seen that the melting temperature of PEAS precursor powders increased with increasing the BIA content in the polymer chains. It mainly due to the incorporation of BIA which gives rise to the rigidity of molecular chain and improves the inter-molecular interaction of the PEAS precursor powders (Fig. 4). Therefore, the presence of BIA units significantly restricts the molecular movement and enhances the resistance during the foaming process of the PEAS precursor powders. As the result, the foaming degree of PEAS precursors powders decreases substantially.

Besides, the precursor powders used for fabricating polyimide foams was produced by crush from solid PEAS resin, resulting in powders size distribution with a wide range. Based on the preliminary investigations,[25] the morphology of precursor particles, such as the size and shape is also an important factor that influencing the foaming process. The bigger particles are conducive to grow into bubbles compare with particles with small size under the given time and heating temperature. This phenomenon is attributed to an increase in specific surface and a reduced nuclear population within the small size particles. As a consequence, a large part of foaming agent evaporated prior to melt of PEAS precursor powders with increasing BIA content in polymer chains, and these powders cannot swell into bubbles at even if the temperature rises to 140 °C. It mainly due to the increase of molecular rigidity that restrict movement of polymer chains. As the result, the PEAS precursor powders could not foam partly or totally as the content of BIA exceeding 50 mol% at the same heating temperature, which remarkably decreases the cell size distribution of the resultant polyimide foams.

3.4 Thermal properties of PI and co-PI foams

The variation in glass transition behavior of polyimide foams was studied using DSC technique. The obtained curves are shown in Fig. 5 and the corresponding T_g values are listed in Table 2. As shown in Fig. 5, the T_g of obtained polyimide foams were mainly located at the range of 257–306 °C, and the incorporation of BIA units exerts a strengthening effect on the T_g values. It is worthwhile to note that the T_g of resultant co-polyimide foams are much higher than of the pristine PI-0. For example, the T_g value of PI-3 is 306 °C which is higher than pristine PI-0 foam at 257 °C, with an increase of nearly about 50 °C. The T_g value is closely correlated with the flexibility of polymer backbone. The presence of BIA units enhanced the rigidity of polymer backbone significantly.[26,27] As a consequence, the T_g of co-polyimide foams shift toward a higher temperature region with the BIA content elevated. On the other hand, the N–H groups in the benzimidazole unites is expected to form strong hydrogen bonding with carbonyl groups of cyclic imide. This inter-molecular interaction would restrict the motion of polymer molecular.[28] As a result, the co-polyimide foams were endowed with higher T_g value.

The thermogravimetric analysis (TGA) can be used to investigate the thermal stability of the resultant co-polyimide foams. Fig. 6 shows the TGA curves of resultant polyimide and co-polyimide foams under nitrogen atmosphere. The temperature at 5% weight loss ($T_d^{5\%}$), the temperature at 10% of weight loss ($T_d^{10\%}$) and the maximal decomposition temperature (T_d^{max}) are summarized in Table 2. As shown in Fig. 6 and Table 2, all polyimide foams thermally degrades in similar fashion in TGA curves, and there is almost no weight loss in the temperature range of 25–400 °C, demonstrating excellent thermal stability. Above 450 °C, weight loss started due to thermal decomposition of polymer chains. The maximum degradation rate of polyimide foams occurs at the temperature of 590–605 °C. Moreover, it is important to note that the $T_d^{5\%}$ of PI-3 reached to 533 °C as the BIA loading up to 30 mol%. The resultant foams displayed a rising trend in thermal stability with increasing the BIA content in the polyimide chains.[29] It has been demonstrated that the presence of BIA units with high rigidity brought better thermal stability to the co-polyimide

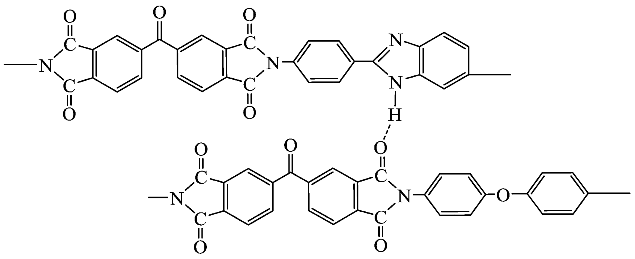


Fig. 4 The inter-molecular hydrogen bonding for co-PI containing benzimidazole units.

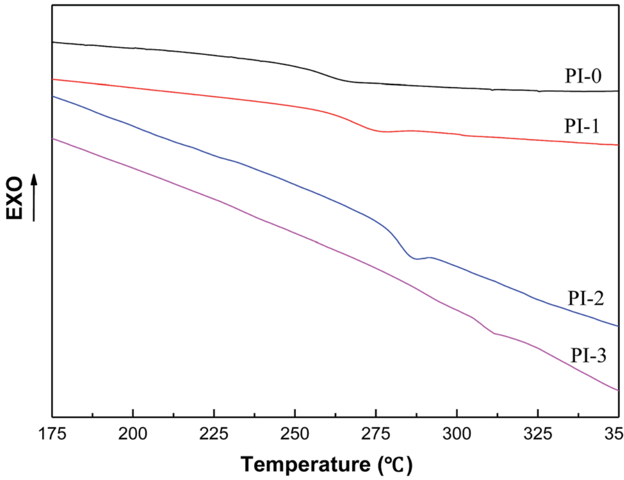


Fig. 5 DSC curves of the PI and co-PI foams.

Table 2 Thermal and mechanical properties of PI and co-PI foams

PI	T_g[a] (°C)	$T_d^{5\%}$ (°C)	$T_d^{10\%}$ (°C)	T_d^{max} (°C)	Compressive strength[b] (MPa)
PI-0	257	515	555	595	0.16 ± 0.03
PI-1	265	522	560	597	0.34 ± 0.02
PI-2	278	525	563	598	0.44 ± 0.05
PI-3	306	533	569	602	0.71 ± 0.09

[a] Determined from the DSC curve at the second heating scan. [b] The compressive strength at 15% compressive deformation.

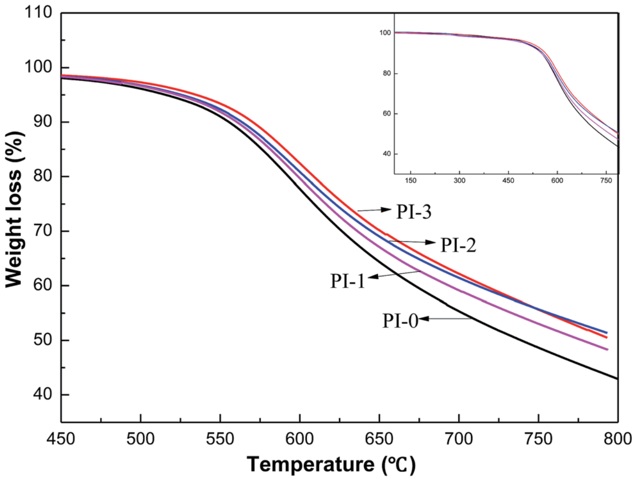


Fig. 6 TGA curves of the PI and co-PI foams.

foams. The incorporation of BIA into the polymer chains improves the thermal stability of co-polyimide foams effectively.

3.5 Mechanical properties of PI and co-PI foams

The influence of BIA on mechanical properties of resultant polyimide foams was also evaluated. The compressive stress–strain curves of resultant polyimide foams are shown in Fig. 7, and the specific data for compressive strength values at 15% strain are summarized in Table 2. It can be seen that co-polyimide foams containing BIA units presented better mechanical properties in comparison with the pristine PI-0 foam. Additionally, the compressive strength and initial modulus of the foams displayed a remarkable upward trend upon incorporating more BIA units into the polymer chains. The compressive strength increased about 4 times as the BIA content increased from 0 mol% to 30 mol% at room temperature. Besides, the observed relationship between strength improvement and increasing foam density is compatible with similar findings available in the literature for flexible foam materials.[30,31] The results are in substantial compliance with law of strength with density. The compressive strength of polyimide foams is mainly related to the foaming degree and its density. In principle, the higher density is beneficial to obtain the foams with higher compressive strength.[32] Furthermore, compared to other solid polyimide materials, it is difficult to speculate the specific influence of molecular rigidity or inherent viscosity on the mechanical strength of polyimide foams, which is mainly due to the low density, different cell shapes and cells' collision of foam materials. However, the resultant co-polyimide foams presented better compressive properties in comparison with commercial pristine polyimide (BTDA–ODA) foams with the same density,[1,2] which demonstrates that BIA plays a positive role in improving the mechanical strength of polyimide foams.

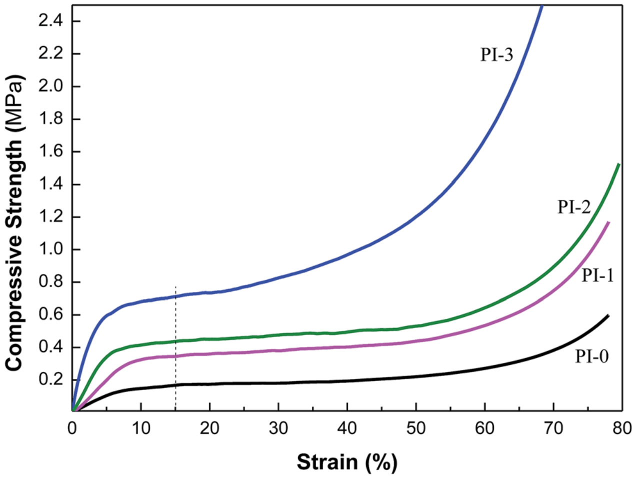


Fig. 7 Compressive properties of the PI and co-PI foams.

4. Conclusion

In summary, a series of co-polyimide foams containing BIA units were prepared successfully through thermal foaming of PEAS precursor powders, which were prepared *via* the reaction of BTDA with BIA and ODA with various molar ratios. The results indicate that the foaming degree of PEAS precursor powders decreases with increasing the BIA content in the polymer chains. Furthermore, the incorporation of BIA units can effectively improve the thermal stability of polyimide foams. The T_g of PI-3 increases around 50 °C in comparison with the pristine PI-0 foam. With the aid of the strong inter- or intra-molecular hydrogen-bonding interactions the co-polyimide foams with higher mechanical strength were resulted. In brief, the physical properties of co-polyimide foams can be adjusted by introducing various content of BIA into the polymer chains. This technique offers a good option to fabricate high-performance polyimide foams with lightweight, high thermal stability as well as enhanced mechanical properties. These co-polyimide foams enrich the variety of high performance polymers and have promising application in the future industries.

Acknowledgements

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