

Effects of 3,4'-Oxydianiline on the Structures and Properties of a Novel Aromatic Polyimide Foam

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ABSTRACT: Aiming at the low volumetric shrinkage, a novel aromatic polyimide foam is successfully prepared from polymethane polyphenyl isocyanate (PAPI) and a poly(amic-acid) precursor which has been synthesized from 3,4'-oxydianiline (3,4'-ODA) and pyromellitic dianhydride (PMDA). In this research, five polyimide foams, with different contents of 3,4'-ODA, are comparatively studied including structural, thermal, mechanical, shrink, and degradation properties. The results indicate that the content of 3,4'-ODA has minor influence on chemical structures, but significant influence on cell structures of the foams. With the increase of

3,4'-ODA, the volumetric shrinkages, apparent densities and the compressive and flatwise tensile strengths of the materials decrease. The glass transition temperatures (T_g) decrease from 301°C to 279°C, and the 5% weight loss temperatures ($T_{5\%}$) increase from 323°C to 340°C. Through TG-FTIR analysis, we can observe that the addition of 3,4'-ODA has no influence on the pyrolysis mechanism of polyimide foams. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polyimide foam; structures; volumetric shrinkage; properties

INTRODUCTION

Since the discovery of outstanding features including light weight, thermal and fire resistance, less smoke generation, no halogen, no ozone consumption, easy installation in polyimide foams, considerable attention has been attracted in this intriguing material.^{1,2} They have been recognized as attractive materials for applications in spacecraft, aircraft, weapon equipments, marine, and high-speed train.³ According to the type of cell structure, the polyimide foams could be classified into closed-cell and open-cell. The closed-cell foams can be prepared through powder foaming process in the following way. A poly(amic-acid) precursor was first prepared by using aromatic diamine and aromatic carboxylic acid at specific mole ratio, and then was dried and ground to powders for forming a uniform, mostly closed cell product.^{4–6} The open-cell foams can be prepared through one-pot process, utilizing small molecules from polycondensation reaction as blowing agent to foam. Polyimide foams with open cells resulted when the mixture of aromatic dianhydride solution and PAPI was poured into open moulds and allowed to rise freely without confining surfaces present to hinder the cell formation.^{7–9} It was also to be noted that the high open cell content was attributed to the release of large amounts of CO₂ and

residual solvents, wherein the volumetric shrinkage that occurred during postcure process was a serious problem. As a consequence, the pronounced raw material waste cannot be avoided. Furthermore, in a composite, the reinforcing material often did not allow appreciable shrinkage in the overall dimension of the molded object to prevent enormous stresses from being built up in the composite.¹⁰ For these reasons, the volumetric shrinkage of polyimide foams must be overcome.

In this research, a novel preparation method based on the combination of one-pot and powder foaming processes was adopted in this article. The conventional open-cell polyimide foams presented crosslink structures. The addition of 3,4'-ODA would introduce the flexible chains into crosslink structure, resulting in higher segment motility and lower volumetric shrinkage. The structural, thermal, mechanical, shrink, and degradation properties of polyimide foams with different contents of 3,4'-ODA were investigated. The results revealed that the content of 3,4'-ODA had significant effects on the structures and properties of polyimide foams. The test data also confirmed that these foams exhibited excellent thermal and mechanical resistance.

EXPERIMENTAL

Materials

PMDA was purchased from Liyang Qingfeng Fine Chemical Plant, China, and dried in a vacuum oven for 6–8 h prior to use. 3,4'-ODA was purchased from

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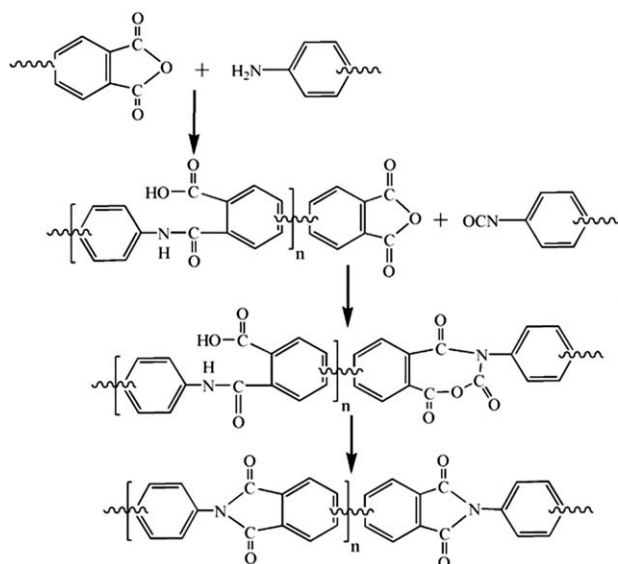


Figure 1 The reaction between poly(amic-acid) and PAPI.

Shanghai Research Institute of Synthetic Resins, China. PAPI was obtained from Yantai Wanhua Polyurethanes Co. Ltd., China. Silicone oil (DC-193) was acquired from Foshan Daoning Chemical Co. Ltd., China, and it was the main surfactant. *N,N*-dimethylformamide (DMF), catalysts (TEOA and DBTDL) and blowing agent (distilled water and MeOH) were supplied by Beijing Finechem.

Preparation

PMDA and 3,4'-ODA were accurately weighed and dissolved in DMF at room temperature. The mixture was stirred for 4–6 h until they completely reacted. DC-193, catalysts, and other additives were then added to the solution and stirred for 1–2 h at 80–120°C to obtain a precursor solution. When the precursor solution was cooled to ~ 25°C, PAPI was added to the precursor solution. The combination of precursor solution and PAPI was stirred with a high speed mixer (about 2000 rpm) for 5–15 s. Then it was transferred to a preheated mould where it was allowed to rise freely. Once the foam was no longer tacky, it was then treated in vacuum oven at 180–250°C for 0.5–4 h to complete the polymerization reactions. The sample without 3,4'-ODA was simplified as PIF-0. The other polyimide foams were prepared by varying the mole ratios of 3,4'-ODA / PMDA from 5/100, 10/100, 15/100, to 20/100. And similarly to PIF-0, these foams were expressed as PIF-1, PIF-2, PIF-3, and PIF-4, respectively.

Characterization

The chemical structures of polyimide foams with different contents of 3,4'-ODA were characterized by

a Nexus-470 Fourier transform infrared spectroscopy (FTIR) instrument. The cell morphologies were observed using a CS-3400 scanning electron microscopy (SEM) measurement. Dynamic mechanical analysis-IV (DMA-IV) was used to carry out dynamic compressive mechanical analysis at a frequency of 1 Hz and a heating rate of 5°C/min in nitrogen. Thermogravimetry analysis (TGA) was carried out with NETZSCH STA TGA-409C at a heating rate of 10°C/min in nitrogen. Compressive and flat-wise tensile strengths were measured on a 5000 kg SANS test stand according to ISO 844 : 2004 and ASTM C297-94 (1999) test C, respectively.

RESULTS AND DISCUSSION

Reaction mechanism

The preparation of polyimide foams utilizing aromatic dianhydride and isocyanate was previously reported.¹¹ This reaction contained the following steps. First, a seven-membered ring was generated from the isocyanate groups (–NCO) and anhydrides. Then, the seven-membered ring was converted to imide ring during the postcure.

In this article, PMDA and 3,4'-ODA were first condensed in DMF to form a poly(amic-acid) solution. Then, polyimide foam was prepared from the condensation of poly(amic-acid) solution and PAPI to form a foam intermediate. Imidization can be accomplished thermally to yield the final products. The synthesis and chemical structures are shown in Figure 1.

Chemical structures of polyimide foams

The FTIR spectra of polyimide foams with different contents of 3,4'-ODA are shown in Figure 2. It can be seen that the addition of 3,4'-ODA has little

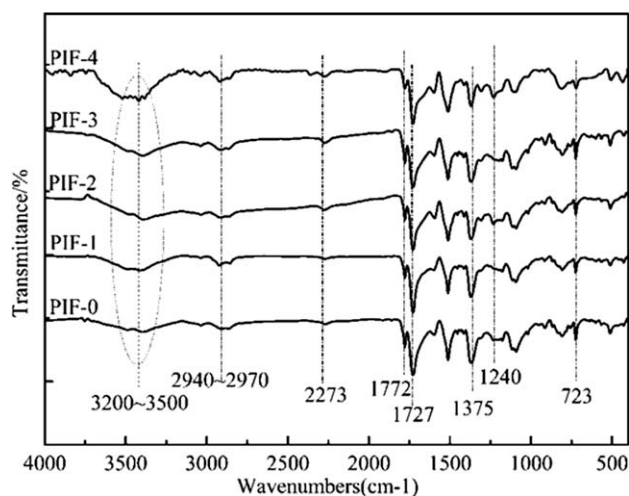


Figure 2 FTIR spectra of polyimide foams with different contents of 3,4'-ODA.

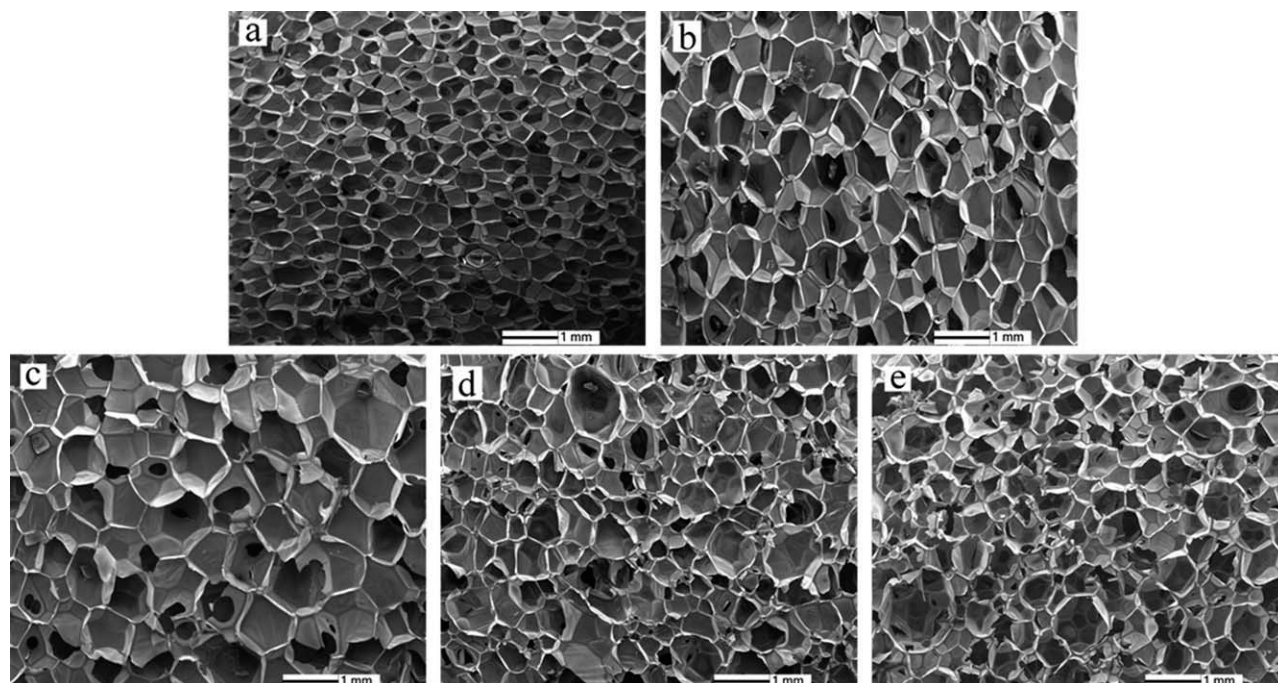


Figure 3 The SEM images of the polyimide foams with different contents of 3,4'-ODA, (a) PIF-0, (b) PIF-1, (c) PIF-2, (d) PIF-3, and (e) PIF-4.

influence on the chemical structures. The broad absorption bands at $2940\text{--}2970\text{ cm}^{-1}$ indicate the existence of $\text{—CH}_2\text{—}$ and —CH— in the organic system. The characteristic absorption peaks at 1772 cm^{-1} (asymmetrical C=O stretch) and 1727 cm^{-1} (symmetrical C=O stretch) indicate the presence of imide carbonyl. The peaks at 1375 cm^{-1} correspond to the C—N stretching vibration of imide rings. The out-of-phase bending of imide ring vibration can be observed at 723 cm^{-1} . There are no characteristic absorption peaks of C=O and C—N in —CONH— at 1654 cm^{-1} and 1538 cm^{-1} , respectively, which indicates that the imidization has been completed. The peaks at 1240 cm^{-1} corresponding to the aromatic ether bond (C—O—C) stretching vibration could be observed in the FTIR spectra of polyimide foams with higher contents of 3,4'-ODA. The broad absorption bands appearing in the range from 3200 cm^{-1} to 3500 cm^{-1} indicate the presence of —NH— unit, associated with urea. With the increasing content of 3,4'-ODA, the amount of unreacted anhydride groups in the precursor solution decreased. Therefore, the amount of —NCO which had reacted with PMDA decreased as well, resulting in the increase of —NH— units generated from —NCO and hydroxy groups (—OH) in the other additives.¹² So the intensities of the absorption peaks at $3200\text{--}3500\text{ cm}^{-1}$ increase in the order of sequence from PIF-0 to PIF-4.

Cell structures of polyimide foams

Identification and characterization of the cross section of five polyimide foams were preformed with a

high-resolution SEM. The cell structures are shown in Figure 3(a–e), respectively. The cellular diameters distribution statistics are presented in Figure 4(a–e). The components and properties of polyimide foams are shown in Table I. As shown in Figure 3, the cells can be clearly observed and are almost hexagonal. Comprehensive analysis shows that the cellular sizes of PIF-0, PIF-1, and PIF-2 distribute in a narrow range with the average cellular diameter of 0.40 mm, 0.49 mm, and 0.68 mm, respectively. Compared with PIF-0, PIF-1 and PIF-2, the cell sizes of PIF-3 and PIF-4 are in a nonuniform distribution. According to the analysis, the more 3,4'-ODA was used, the less unreacted PMDA was left, leading to more PAPI left in the precursor solution. The CO_2 derived from the reaction of residual PAPI and H_2O was the main blowing agent for the foaming process. The increased release rate and amount of CO_2 resulted in larger cellular diameters.^{13,14} When less 3,4'-ODA was adopted, precursor solution with low viscosity can mix with PAPI homogeneously, resulting in uniform foaming and well-distributed cellular diameters. When the content of 3,4'-ODA increased to a certain extent, the high viscosity of precursor solution would give rise to inhomogeneous mixing and unsatisfied distribution.

Volumetric shrinkages of polyimide foams

The volumetric shrinkage was one of the most important properties of the polyimide foams. The values of volumetric shrinkages and apparent

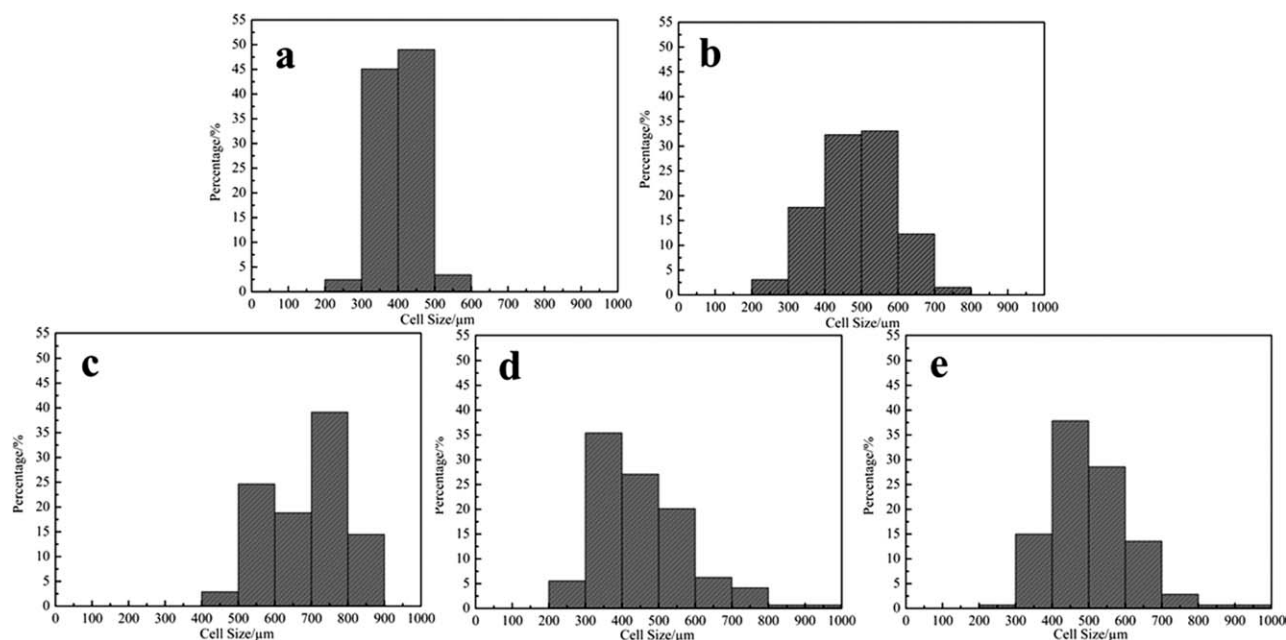


Figure 4 The cellular diameters distribution statistics of the polyimide foams with different contents of 3,4'-ODA, (a) PIF-0, (b) PIF-1, (c) PIF-2, (d) PIF-3, and (e) PIF-4.

densities of polyimide foams with different contents of 3,4'-ODA are shown in Figure 5. The volumetric shrinkages of polyimide foams can be calculated with the following equation:

$$V_0 = \frac{V_1 - V_2}{V_1} \times 100\%,$$

where V_1 is the volume of polyimide foam before postcure, V_2 is the volume of polyimide foam after postcure, V_0 is the volumetric shrinkage. The values of volumetric shrinkages are listed in Table I.

It can be seen that with the increase of 3,4'-ODA, the volumetric shrinkages of polyimide foams decrease. Furthermore, the volumetric shrinkages of PIF-3 and PIF-4 are negative, implying the two foams expand. And even some surface breakages can be observed on PIF-4 because of the larger

expansion. It was believed that the cross-linked structure generated from PMDA and PAPI caused significant volume shrink due to the thermal imidization, while the flexible segments derived from PMDA and 3,4'-ODA had higher motility which resulted in the expansion effect during the postcure. Compared with PIF-3, PIF-4 has a smaller expansion ratio. The reason was that when the content of 3,4'-ODA increased to a certain extent, the tension force derived from the expansion surpassed the surface strength, which caused the surface breakages and the smaller expansion ratio.

As shown in Figure 5 and Table I, the apparent densities of polyimide foams decrease with the increase of 3,4'-ODA. It may be attributed to the decrease volumetric shrinkages of foams with the equivalent mass. Compared with PIF-3, however, PIF-4 has a larger apparent density. That was

TABLE I
The Components and Properties of Polyimide Foams

Polyimide foam	PIF-0	PIF-1	PIF-2	PIF-3	PIF-4
Mole ratio of 3,4'-ODA /PMDA	0	5/100	10/100	15/100	20/100
Volumetric shrinkage (%)	33.4	22.83	9.44	-25.62	-16.48
Apparent density (kg/m ³)	22.60	21.01	18.40	14.76	15.88
Average cellular diameter (mm)	0.40	0.49	0.68	0.45	0.50
T_g (°C)	301.1	297.0	291.4	282.3	279.8
$T_{5\%}$ (°C)	323.0	328.0	337.5	344.5	339.9
$T_{10\%}$ (°C)	368.5	370.9	382.2	390.0	379.5
Wt (%) ^a	44.2	44.4	44.7	45.0	44.9
Compressive strength (KPa)	28.7	27.3	26.2	23.9	23.3
Tensile strength (KPa)	98.7	82.9	67.4	52.9	58.0

^a Residual weight in TGA at 800°C in nitrogen atmosphere.

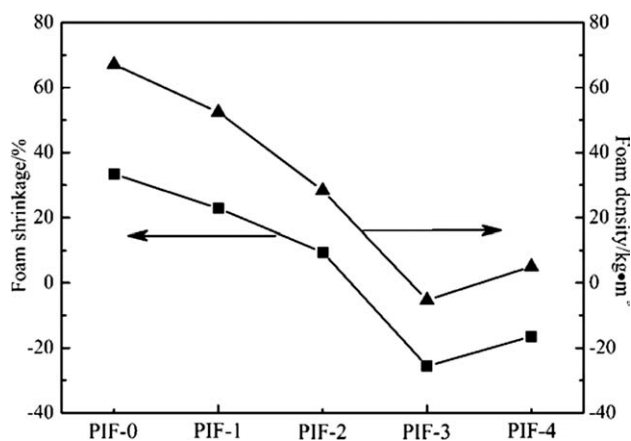


Figure 5 The volumetric shrinkages and apparent densities of polyimide foams with different contents of 3,4'-ODA.

because some surface breakages occurred in PIF-4, and the expansion ratio of PIF-4 was smaller than PIF-3's.

Thermal properties of polyimide foams

The thermal properties of polyimide foams with different contents of 3,4'-ODA were evaluated by DMA (Fig. 6) and TGA (Fig. 7). As shown in Figure 6 and Table I, T_g values of these polyimide foams are all above 270°C. With the increase of 3,4'-ODA, the T_g values decrease. According to the reaction mechanism, there were cross-linked reactions between PMDA and PAPI. The addition of 3,4'-ODA increased the proportion of flexible thermoplastic chains, resulting in low T_g values.

TGA and differential thermogravimetric (DTG) curves of polyimide foams with different contents of 3,4'-ODA are represented in Figure 7 and Figure 8, respectively. $T_{5\%}$ and $T_{10\%}$ values of these polyimide foams are all above 320°C and 365°C, respectively,

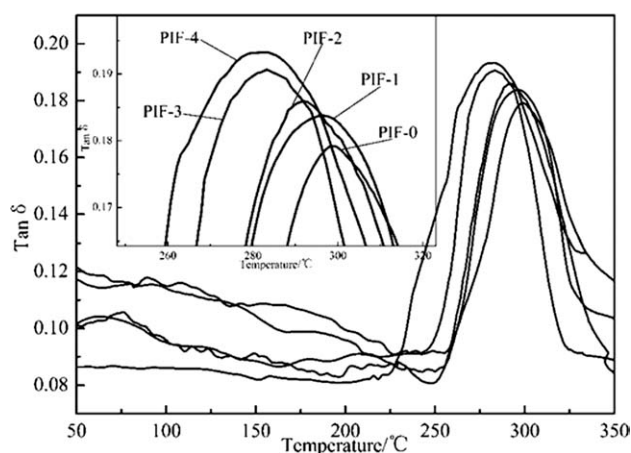


Figure 6 DMA curves of polyimide foams with different contents of 3,4'-ODA.

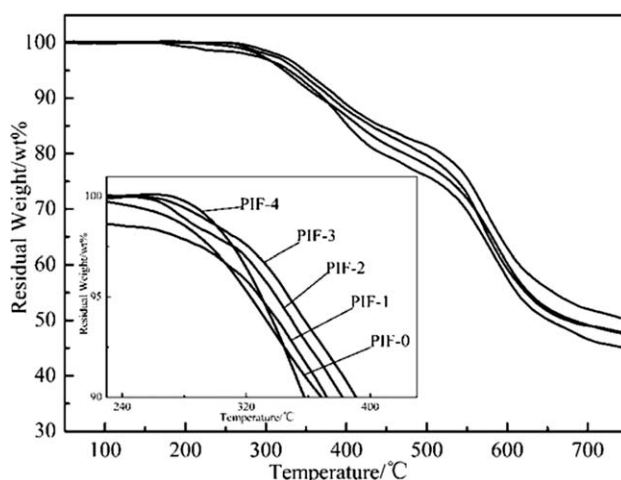


Figure 7 TGA curves of polyimide foams with different contents of 3,4'-ODA.

and the residual weight rates are more than 45% at 800°C, as shown in Figure 7. These data indicate that polyimide foams in this study have excellent thermal stability. The $T_{5\%}$ values of polyimide foams increase with the increase 3,4'-ODA, except for PIF-4. Through further analysis, the unstable carboxylic acid end groups can decompose into CO_2 . The poly(amic-acid) generated from 3,4'-ODA and PMDA could cause the decrease of unstable carboxylic acid end groups and the increase of imide ring after postcure.¹⁵

As shown in Figure 8, there are two decomposition regions for all the samples. The first region ranges from 265 to 485°C, and the second ranges from 510 to 660°C. Volatilization of residual small molecules and decomposition of unstable segment mainly occurred in the first region. The primary cause for the formation of the second region was the

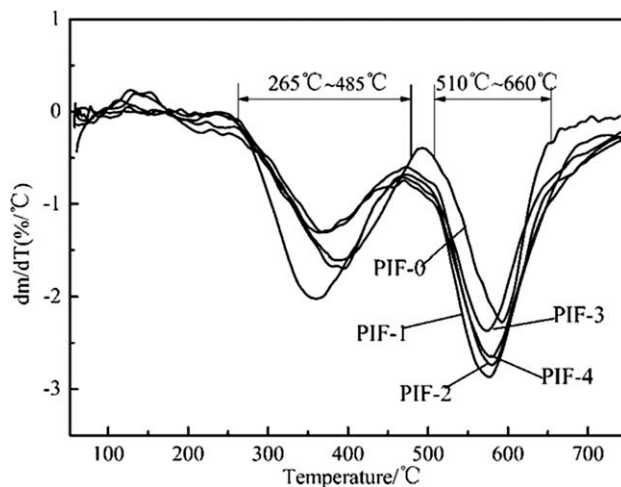


Figure 8 DTG curves of polyimide foams with different contents of 3,4'-ODA.

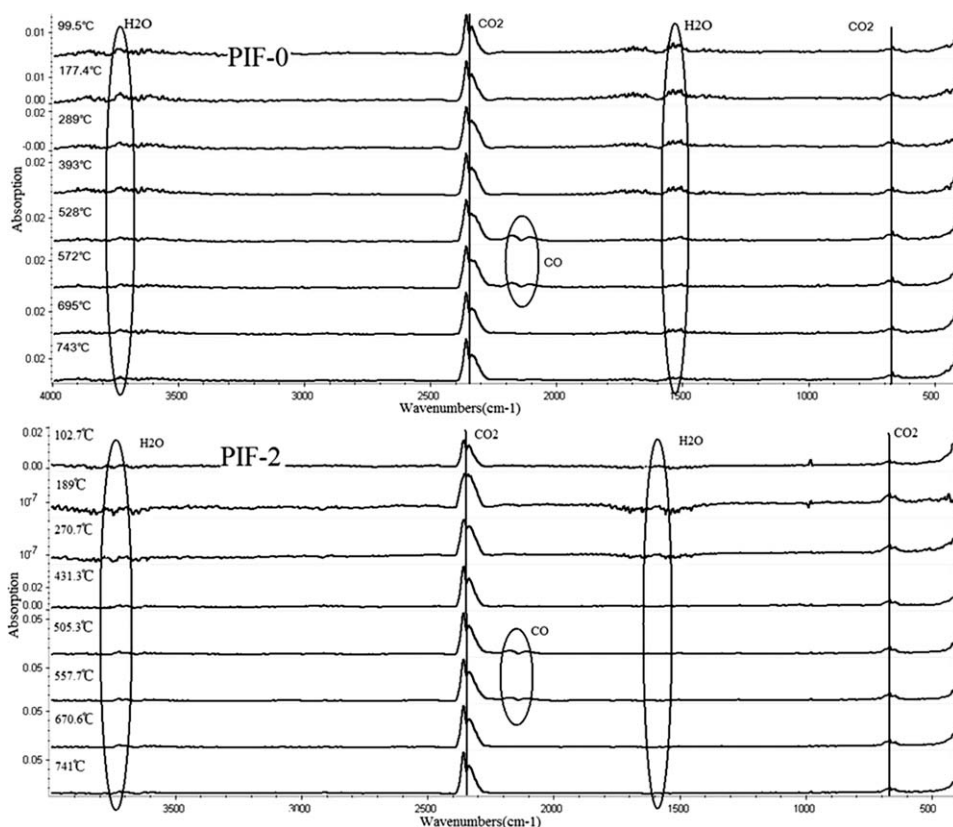


Figure 9 Stacked plot of the FTIR spectra of by-products from the TG-FTIR of PIF-0 and PIF-2.

decomposition of imide ring. This can be further confirmed by the TG-FTIR analysis.

The thermal decomposition behaviors of polyimide foams were investigated by TG-FTIR under nitrogen atmosphere at a heating rate of 10°C/min. Stacked plot of the FTIR spectra of thermal decomposition products of PIF-0 and PIF-2 under nitrogen are shown in Figure 9, respectively. The characteristic bands of CO₂ which appear during the whole heating process are at 2355 cm⁻¹ and 690 cm⁻¹. Meanwhile, the characteristic band of CO is at 2181 cm⁻¹ and emerges in the range of 510–660°C with low absorption intensity. In addition, weak H₂O absorption peaks are detected during the whole decomposition process, and they may be mainly attributed to desorption at lower temperature and decomposition of the unstable groups at higher temperature. In the course of thermal decomposition, CO₂ evolved at low temperature was attributed to desorption or weak bound species. At higher temperatures, CO₂ was attributed to decarboxylation of acid, uncyclized amic acid, or/and anhydride end groups. The dimerization of isocyanate yielding a carbodiimide and the rearrangement of an imide to an isoimide were both followed by the thermal release of CO₂. The thermal decomposition of imide ring, carbonyl and ether in main chain with the release of CO occurred in the range of 500–

700°C.^{16,17} From the above, a conclusion can be drawn that PIF-0 and PIF-2 have the same pyrolysis mechanism.

Mechanical properties of polyimide foams

The compressive strengths at 10% compressive deformation and flatwise tensile strengths of polyimide foams decrease with the increase content of 3,4'-ODA, as shown in Figures 10 and 11, respectively.

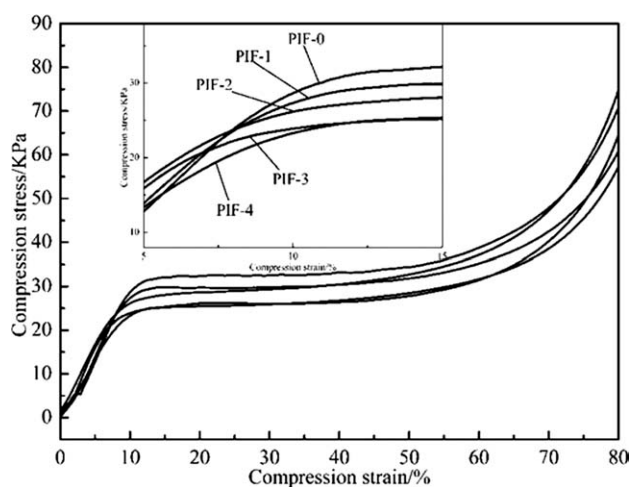


Figure 10 Compressive stress–strain curves of polyimide foams with different contents of 3,4'-ODA.

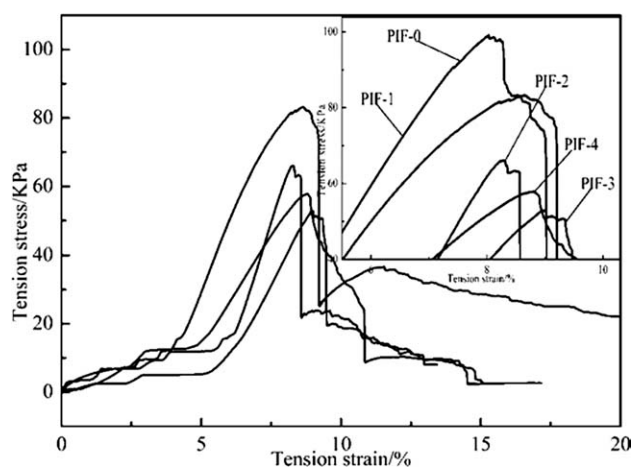


Figure 11 Tensile stress–strain curves of polyimide foams with different contents of 3,4'-ODA.

And the test data are given in Table I. According to the analysis, the main factors contributing to the mechanical properties of polyimide foams were apparent densities and cell structures. It was found that polyimide foams with higher densities had smaller average cellular diameters and thicker cell edges which resulted in greater compressive and flatwise tensile strengths.¹⁸ Furthermore, the apparent densities of polyimide foams decrease with the increase content of 3,4'-ODA, as shown in Table I. So the increase of 3,4'-ODA led to the mechanical properties reduction of the foams.

CONCLUSIONS

Polyimide foams with different contents of 3,4'-ODA were successfully prepared from PAPI and poly (amic-acid) precursor which had been synthesized from 3,4'-ODA and PMDA.

1. The addition of 3,4'-ODA had minor impact on the chemical structures of polyimide foams with and without 3,4'-ODA.
2. The cell structures of foams were uniform when small amount of 3,4'-ODA was used, while poor homogeneity when 3,4'-ODA was excess. The cellular diameters increased, with the increase of 3,4'-ODA.
3. With the increase of 3,4'-ODA, the volumetric shrinkages and apparent densities decreased.

4. Polyimide foams presented excellent thermal stability with T_g values in the range of 279–301°C and $T_{5\%}$ values in the range of 323–345°C. T_g values increased while $T_{5\%}$ values decreased when the content of 3, 4'-ODA increased. The residual weight rates of the foams were more than 45% at 800°C. Through TG-FTIR analysis, we know that PIF-0 and PIF-2 had the same degradation process, indicating 3,4'-ODA exerted no influence on the pyrolysis mechanism of polyimide foams.
5. The compressive and flatwise tensile strengths of polyimide foams decreased with the increase of 3,4'-ODA, which was consistent with the apparent densities.

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