

Preparation and Properties of Rigid Polyimide Foams Derived from Dianhydride and Isocyanate

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ABSTRACT: A series of rigid polyimide (PI) foams were synthesized via the reaction of a first solution with a second solution. The first solution was isocyanate-terminated polyimide prepolymers; the second solution contained deionized water and surfactant. The effect of different water contents and isocyanate index on the structures and properties of rigid PI foams were investigated. The apparent density, hardness, compressive strength, and the 5% weight loss temperatures ($T_{5\%}$) decreased with the increase of water content. With the increase of isocyanate index, the apparent density and the $T_{5\%}$ values decreased, whereas the glass transition temperatures (T_g) increased and the hardness, compressive strength first increased and then decreased. The rigid PI foams composed of closed-cells were confirmed by scanning electron microscopy. The maximum compressive strength of rigid PI foams prepared was up to 1.31 MPa. Moreover, excellent thermal stability was presented with the $T_{5\%}$ values were all above 360°C and the residual weights of the foams (R_w) were more than 50% at 800°C. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Polyimide (PI) foams have some outstanding properties such as thermal resistance, low smoke generation, no ozone consumption, halogen free, and so on.^{1,2} They have been used in many applications such as heat-resistance materials, weight-reduction materials, thermal insulation materials, and supporting structure materials.^{3,4} Aviation and spacecraft are built by lightweight, high-strength materials due to it is very sensitive to quality. PI foams are one of the best candidate materials. However, except for the rigid Rohacell[®] PMI foams, the compression strength of other PI foams can not satisfy the high-strength requirement of aviation and spacecraft, thereby increasing the compressive strength of the PI foam is extremely important.⁵

The ever-reported rigid PI foams included: (1) TEEK foams prepared by NASA. They were prepared by powder foaming process. However, the molding process was very complex and the compressive strength was unsatisfactory.^{6–8} (2) Rohacell[®] PMI foams. The high-performance PMI foams can meet the demands for building aviation and spacecraft. The excellent creep compression resistance of PMI foams makes it possible to use them for cure cycles. However, its heat distortion temperature was only 180°C, which restricted its application.^{3,9–12} (3) Rigid PI foams prepared from aromatic dianhydrides and isocyanates.^{13–18} Some United States patents, such as US 3,300,420 and US 4,184,021, had

reported a simple method to prepare rigid PI foams. These rigid PI foams were prepared through one-step process, using small molecules generated by this reaction as blowing agent, such as carbon dioxide (CO₂) generated by the polycondensation of dianhydride and isocyanates. However, there are few systematic reports for the study of relationships among compositions, structures, and properties of these rigid PI foams.

Aiming at the high mechanical properties and easily prepared PI foams, the preparation and characterization of rigid PI foams derived from the reaction of the isocyanate-terminated PI prepolymers and deionized water are presented in this article. The focus of this work is to compare structures and properties of the PI foams in terms of different water contents and isocyanate index. The results showed that water content and isocyanate index had great effect on the structures and properties of these PI foams. The test data can also confirm that these foams possess excellent mechanical and thermal properties.

EXPERIMENT

Materials

Pyromellitic dianhydride (PMDA) was purchased from Liyang Qingfeng Fine Chemical Plant, China, and used after drying at 150°C. Polyaryl polymethylene isocyanate (PAPI) was obtained from Yantai Wanhua Polyurethanes, China. Surfactant (AK8805)

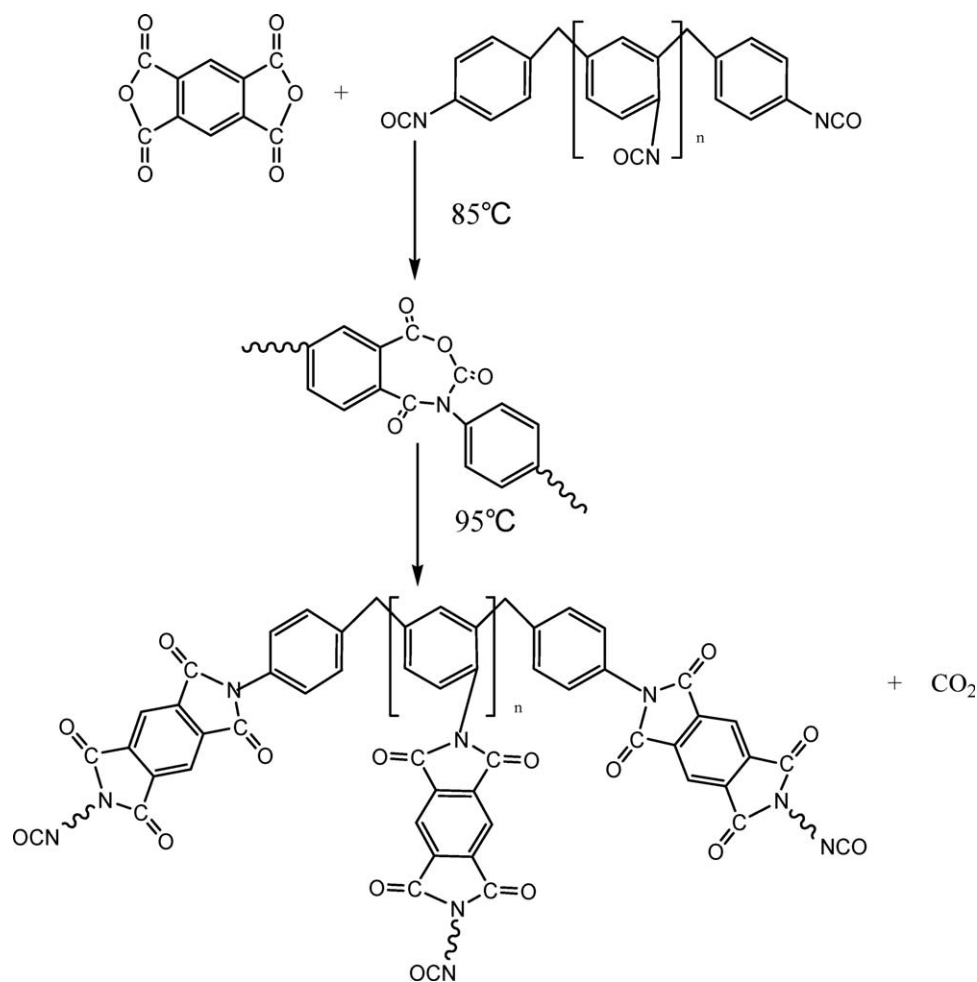


Figure 1. The reaction between anhydride and excess isocyanate.

was acquired from Nanjing Dymatic Shichuang, China. *N,N*-dimethylformamide (DMF), deionized water (H₂O) and methanol were supplied by Beijing Finechem.

Preparation

PMDA was accurately weighed and dissolved in DMF at approximately 80°C. The solution was held at 80°C and stirred until PMDA was completely dissolved. Then, the weighed PAPI were added to the DMF solution and stirred for about 2 h at 80°C. The reaction mixture was further heated to 90°C and maintained for 3 h to obtain a first solution. The first solution was cooled to 30°C. Once cooled, deionized water and surfactant as the second solution were added to the first solution. The combined first solution and the second solution were stirred with a high speed mixer (about 2000 rpm) for approximately 60–120 s. After that it was put into the closed mold which size was 200 mm × 200 mm × 30 mm to form the intermediate. The intermediate was then treated in microwave oven. Finally, it was placed in a vacuum oven at 180–250°C and cured for 0.5–4 h to complete the imidiation. The prepolymers with different isocyanate indexes were synthesized by different molar ratios of PMDA and PAPI. Rigid PI foams with different water contents were prepared by varying the mass ratio of H₂O/PMDA from 5/100, 6/100, 8/100–10/100, and 12/100 and were marked by PIF-

1, PIF-2, PIF-3, PIF-4, and PIF-5, respectively. Similarly, PI foams with different isocyanate index (R = isocyanide carboxylic (–NCO)/Anhydride) : 1.12, 1.19, 1.28, 1.36, 1.43 were marked by PIF-6, PIF-7, PIF-8, PIF-9 and PIF-10, respectively.

Characterizations

Apparent density was tested according to ISO 845: 2006. The chemical structures of the rigid PI foams were characterized by Nexus-470 Fourier transform infrared spectroscopy. The cell morphologies of these foams were observed using a CS-3400 scanning electron microscopy (SEM). The 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. Thermogravimetric analyzer (TGA) was carried out with NETZSCH STA TGA-409C at a heating rate of 10°C/min in nitrogen. Compressive strengths were measured on a 5000 kg SANS mechanical testing machine following ISO 844: 2004 and the dimensions of the samples were 50 mm × 50 mm × 15 mm. Hardness values of PI foams were tested according to ASTM D2240 on a HT-6510C shore durometer.

Reaction Mechanism

Synthesis of Isocyanate Terminated PI Prepolymers. Isocyanate-terminated PI prepolymers were prepared from aromatic

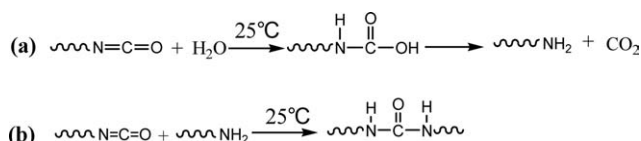


Figure 2. (a) The reaction between ---NCO and water, (b) Secondary reaction of ---NCO .

dianhydride and excess isocyanate via the one-pot process. It included the formation of a seven-membered ring generated from the isocyanide carboxylic (---NCO) and anhydride and the formation of imide ring after postcure. The reaction between anhydride and excess isocyanate is shown in Figure 1.

Foaming Reaction. The foaming reaction and secondary reaction of ---NCO are shown in Figure 2. Foaming reaction in this research referred to the reaction between isocyanide carboxylic (---NCO) and water and the secondary reaction of ---NCO referred to the further reaction between amine (---NH_2) and ---NCO .

RESULTS AND DISCUSSION

Chemical Structures of Isocyanate-Terminated PI Prepolymers

The Fourier transform infrared spectroscopy (FTIR) spectra of the isocyanate-terminated PI prepolymers with different storage time are shown in Figure 3. As shown in Figure 3, the absorption peaks of ---NH--- group near $3200\text{--}3500\text{ cm}^{-1}$ increase and ---NCO groups near 2277 cm^{-1} decrease with the increase of storage time, which may be attributed to the reaction between isocyanate groups and moisture in air. The other characteristic absorption peaks of PI prepolymers with different storage time are similar. The peaks at the range of $2940\text{--}2970\text{ cm}^{-1}$ are due to the vibration of ---CH_2 and ---CH chain formation in isocyanate groups of the organic system. The band at 1659 cm^{-1} can be attributed to the vibrations of C=O in ---CONH--- ; this is due to the secondary reaction of ---NCO .¹⁹ The C=O of imide ring stretching frequency appears at 1778 cm^{-1} and 1727 cm^{-1} .

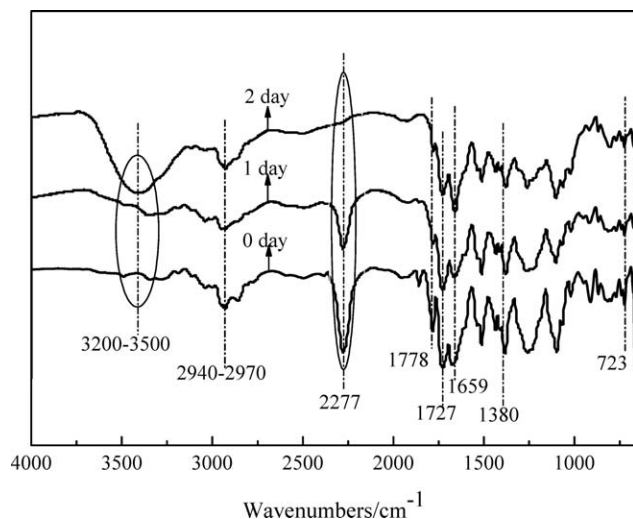


Figure 3. Chemical structures of isocyanate-terminated PI prepolymers.

The peak at 1380 cm^{-1} represents the C---N stretching vibration of imides rings. The out of phase bending of the imide ring vibration can be observed at 723 cm^{-1} .

Chemical Structures of Rigid PI Foam

Figure 4 illustrates the FTIR spectra of rigid PI foam before and after postcure. The imide rings characteristic absorption peaks for rigid PI foams are similar with PI prepolymers. The absorption peaks of ---NCO group near 2278 cm^{-1} decrease and ---NH--- group near $3200\text{--}3500\text{ cm}^{-1}$ increase after postcure; this can be attributed to the imidization reaction. There are no isocyanate absorption peaks at 2278 cm^{-1} for PI foam, which suggests that the reaction between PI prepolymers and the water are complete.

Cell Structures of Rigid PI Foams

The closed-cell structures of rigid PI foams after postcure were confirmed by SEM, as shown in Figure 5. The average cell sizes of rigid PI foams were determined from 40 cells and it increases from $106.2\text{ }\mu\text{m}$ to $159.1\text{ }\mu\text{m}$ with the increase of water content as shown in Table I. The reason for closed-cell can be explained in following way: the PI prepolymers have a high viscosity and strength, during the foaming processes, the cells first expand with gases (including CO_2 and residual solvents) inside of the closed cells. As the gases expand they exert pressure on the cell walls and change the shape and size of the cells; however, the gas pressure is less than the strength of the prepolymer, so the gases cannot release from the foam surface.

The Effect of Water Content on the Properties of Rigid PI Foam

The Effect of Water Content on Foam Apparent Density. Rigid PI foams were prepared at isocyanate index 1.28 and at $\text{H}_2\text{O}/\text{PMDA}$ mass ratio from 5/100, 6/100, 8/100–10/100, 12/100 determined according to recent study. The effect of deionized water as a chemical blowing agent on apparent density is revealed in Figure 6. As show in Figure 6, the apparent density decreases from $119.9\text{ kg}\cdot\text{m}^{-3}$ to $68.4\text{ kg}\cdot\text{m}^{-3}$ with the increase of deionized water content. Equal quantities of PAPI

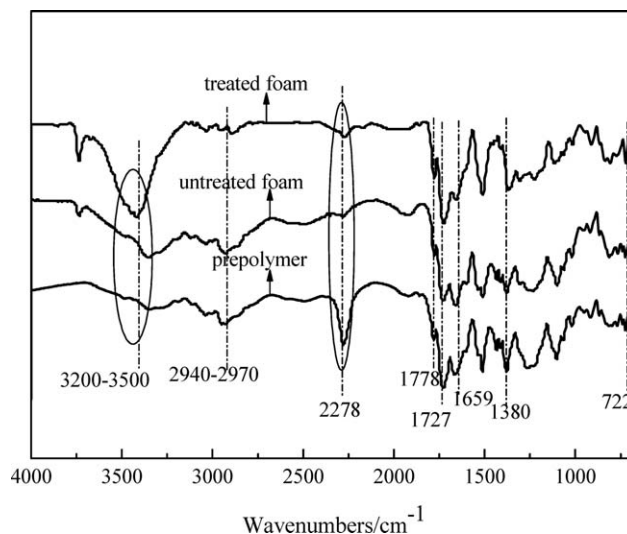


Figure 4. Chemical structures of rigid PI foams.

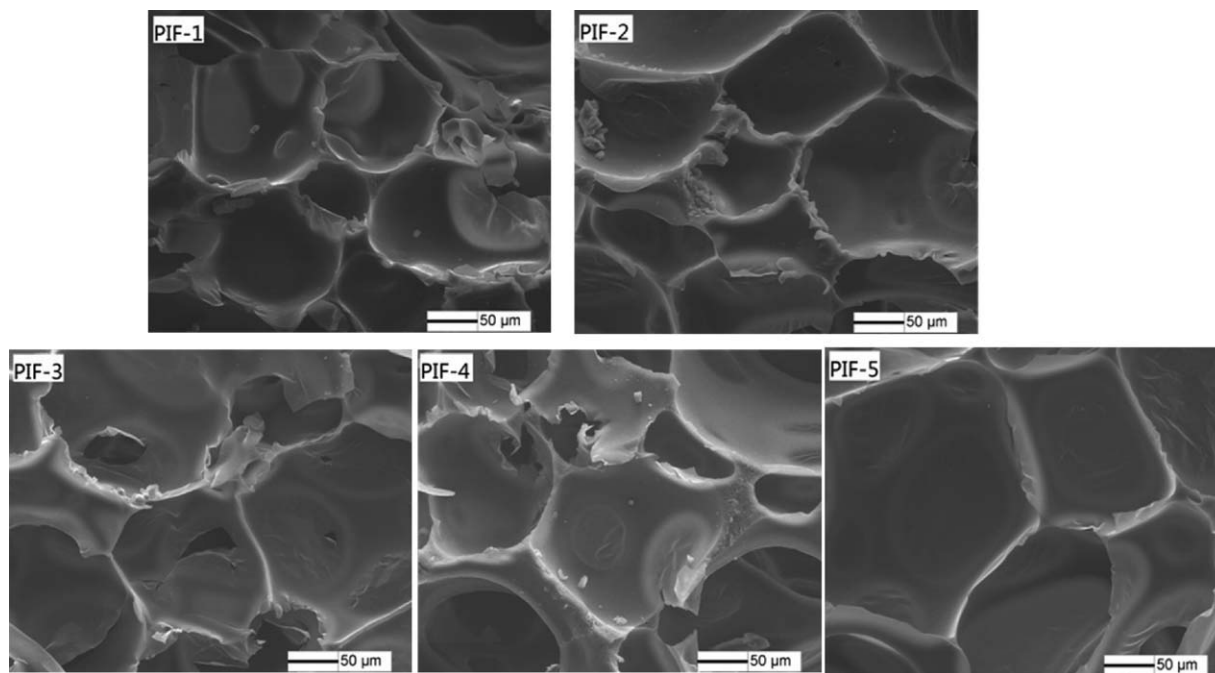


Figure 5. The SEM images of the rigid PI foams with different water contents.

were used for the five PI Foams, while the water content increased the reaction between the water and PAPI are more rapid and complete and the released amount of CO₂ increases. Therefore, more bubbles were generated, and they coagulated with each other. Hence, the cell size of the foam increases and the foam densities decrease with the increase of water content.

The Effect of Water Content on Foam Hardness and Compressive Strength. The effect of water content on foam hardness and compressive strength are shown in Figures 6 and 7, respectively. As displayed in Figures 6 and 7, the compressive strength at 15% compressive deformation decreased from 0.86 to 0.29 MPa and hardness decreased from 84.6 to 69.1 HC with the increase of water content. The mechanical properties and hardness of rigid PI foams are mainly affected by chemical structure, cell structure, cell size, and density. As shown in Figure 5, the rigid PI foams are all closed-cell. For the foams with the same chemical structure and cell structure, higher densities mean smaller cellular diameters and thicker cell edges and walls. Rigid PI foams with higher densities and smaller cellular diameters possess higher compressive strengths and hardness than the one with lower densities, larger average cellular diameters.

Thermal Properties of PI Foams with Different Water Content. The thermal properties of the PI foams with different water contents were evaluated by TGA [Figure (8a)]. The temperature corresponding to the maximum decomposition (T_{max}) of the foams can be determined from differential thermal gravity (DTG) curves. [Figure (8b)]. The 5% weight loss temperatures ($T_{5\%}$) and residual weight retentions (R_w) at 800°C of the PI foams are presented in Table I.

The results of TGA/DTG analysis indicate that the five PI foams have excellent thermal decomposition stability. $T_{5\%}$ values of all foams are more than 360°C and the R_w values are more than 50% at 800°C. It is not obvious that $T_{5\%}$ values change with water content in the Figure (8a). However, as shown in Table I, the $T_{5\%}$ values of PI foams decrease from 385.8°C to 366.6°C with the increasing of water content. Through further analysis, the water could react with $-NCO$ to produce urea bond, the unstable urea bond could be decomposed into CO₂ at 300°C. With increasing of water content, more urea bond was generated, which led to the decrease of $T_{5\%}$ values.

The DTG profiles of PI foams are illustrated in Figure (8b). The five PI foams have similar pyrolysis behaviors in nitrogen,

Table I. The Properties of PI Foams with Different Water Content

PI foam	Density/ kg·m ⁻³	Cell size/ μm	Compressive strength/ Mpa	Hardness/ HC	$T_{5\%}$ / °C	R_w / %
PIF-1	119.91	106.20	0.86	84.62	385.81	55.34
PIF-2	116.22	124.71	0.68	81.44	375.22	55.19
PIF-3	94.43	135.85	0.61	77.67	369.60	54.52
PIF-4	79.13	147.17	0.43	73.46	368.51	53.31
PIF-5	68.41	159.29	0.29	69.13	366.64	52.74

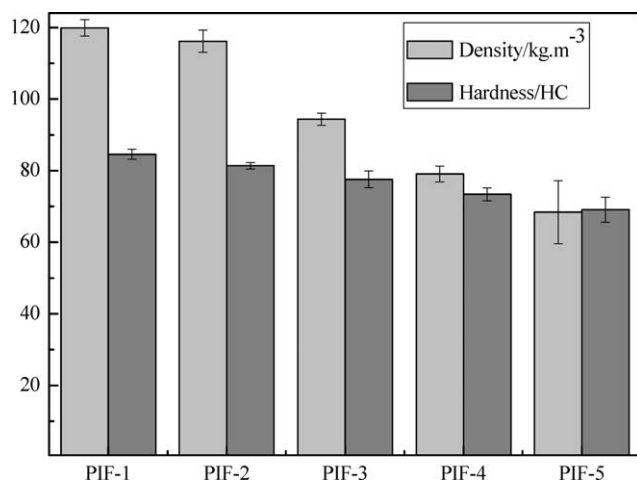


Figure 6. Density and hardness of PI foams with different water contents.

where two characteristic temperature regions are observed. The first region ranges from 275°C to 461°C, and the second ranges from 494°C to 729°C. The volatilization of residual small molecules and the decomposition of unstable end groups mainly occur in the first region, and imide ring decomposes in the second section.¹⁹

The Effect of Isocyanate Index on Properties of Rigid PI Foams

The Effect of Isocyanate Index on Foam Apparent Density. Rigid PI foams were prepared at H₂O/PMDA mass ratio 6/100 and at isocyanate index from 1.12 to 1.43 determined according to recent study. It was found that the foam densities are not very sensitive to isocyanate index, as shown in Figure 9. The densities of the PI foam samples decrease slowly from 120.1 kg · m⁻³ to 116.2 kg · m⁻³, and then decrease rapidly to 65.7 kg · m⁻³. Isocyanate is not only involved in foaming reaction but also participate in polymerization and crosslinking reaction. At first, the main function of isocyanate was as monomer and crosslinker, so the foam density changes little. When isocyanate

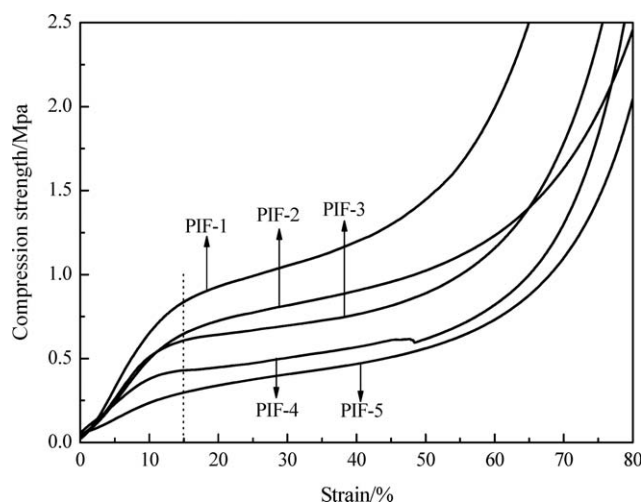


Figure 7. Compressive stress-strain curves of rigid PI foams with different water contents.

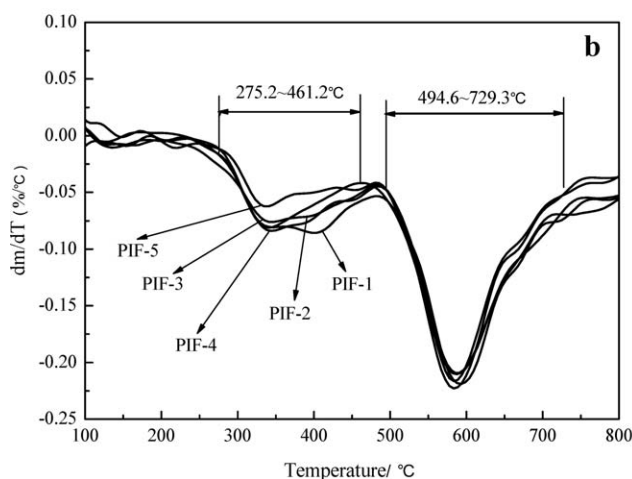
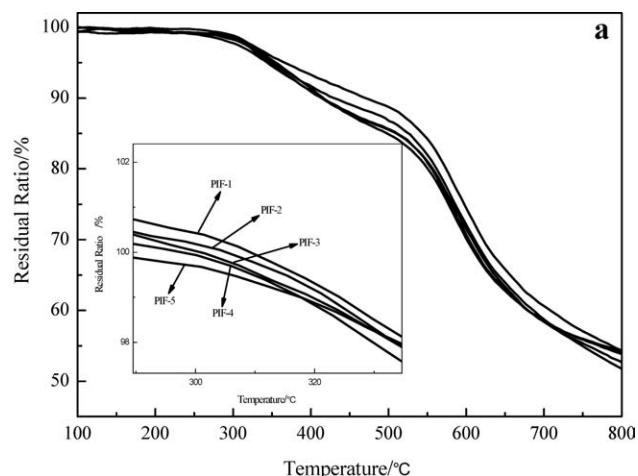


Figure 8. TGA (a) and DTG (b) curves of rigid PI foams with different water contents.

index increase to 1.43, the excess isocyanate groups may react with water to produce more CO₂ which led to the rapidly decrease of density.

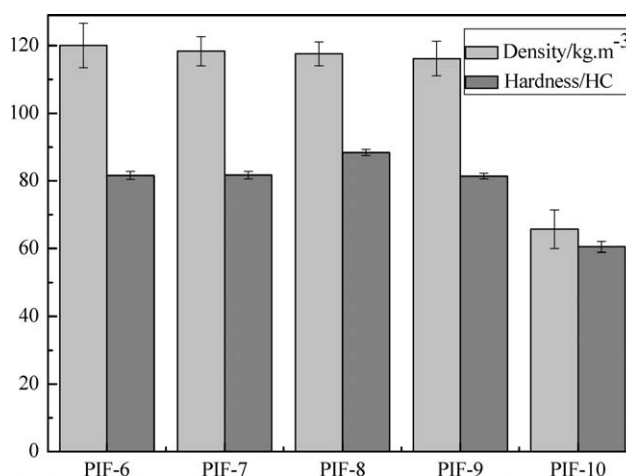


Figure 9. Density and hardness of rigid PI foams with different isocyanate index.

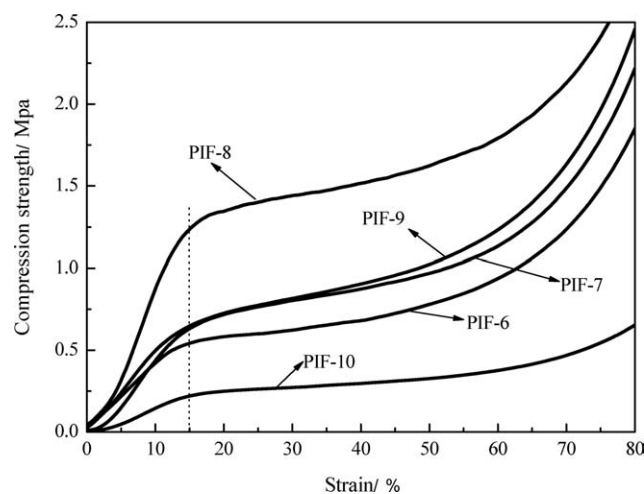


Figure 10. Compressive stress-strain curves of rigid PI foams with isocyanate index.

The Effect of Isocyanate Index on Foam Hardness and Compressive Strength. The effect of isocyanate index on foam hardness and compressive strength were illustrated in Figures 9 and 10 respectively. It is found that up to 1.28 isocyanate index, the compressive strength at 15% compressive deformation and hardness of the samples increase as isocyanate index increase, then it starts to decrease with further increase in isocyanate index, as shown in Table II. The mechanical properties of rigid PI foams with different isocyanate index are mainly affected by the chemical structure. Rigid PI foams prepared from PMDA and PAPI possess the crosslinked structure. At first, up to 1.28 isocyanate index, the crosslinked points of rigid PI foams increase with the increase of isocyanate index, which lead to the increase of the material stiffness and the enhance of compressive strength. Then the further increase in isocyanate index led to the foam excessive crosslinking and the rapidly decrease of density, which makes PI foams become brittle and their compressive strength decrease.

Thermal Properties of PI Foams with Isocyanate Index. The thermal properties of rigid PI foams were studied using DMA and TGA techniques. The temperature at which the maximum of loss tangent ($\tan\delta$) observed is commonly defined as the T_g value by DMA test.

Figure 11 displays the DMA curves of PI foams with different isocyanate index. With the increase of isocyanate index, the T_g values increase from 294.9°C to 315.6°C, as shown in Table II.

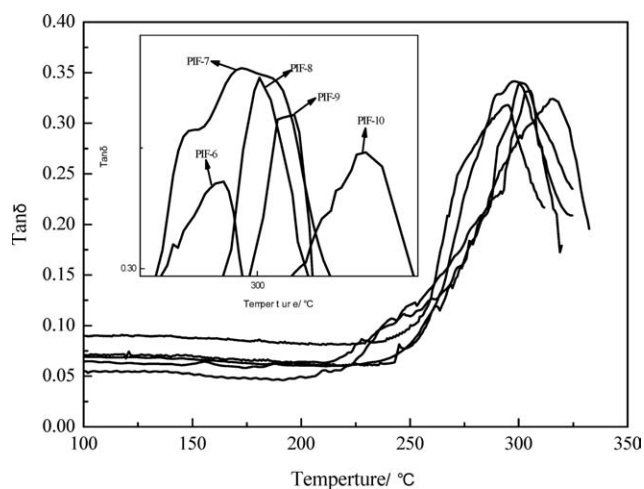


Figure 11. DMA curves of rigid PI foams with different isocyanate indexes.

The reason for this result can be explained in the following way: the crosslinked points of rigid PI foams increase with the increase of isocyanate index, so the average chain length between adjacent crosslinking points became smaller and the polymer free volume decrease, which led to the increase of T_g value.

TGA and DTG curves of rigid PI foams with different isocyanate index are represented in Figure (12a) and (12b). From Figure (12a) and Table II, we can clearly see that $T_{5\%}$ values of these PI foams are all above 360°C. And the residual weight rates (R_w value) are more than 50% at 800°C. These data indicate that rigid PI foams in this study have excellent thermal stability. The $T_{5\%}$ values of PI foams decrease from 452.3°C to 368.9°C with the increasing of isocyanate index. The reason may also was the unstable urea bond could be decomposed into CO_2 at 300°C and the $-\text{NCO}$ can react with water to produce urea bond. More urea bond was generated with the increase of isocyanate index, which led to the decrease of thermal stability.

The DTG profiles of PI Foams are illustrated in Figure (12b). The five PI Foams have similar pyrolysis behaviors in nitrogen, where two characteristic temperature regions are observed. The first region ranges from 293.5°C to 470.6°C, and the second ranges from 482.5°C to 711.4°C. The volatilization of residual small molecules and the decomposition of unstable groups (urea) mainly occur in the first region, and imide ring decomposes in the second section.

Table II. The Properties of PI Foams with Different Isocyanate Index

PI Foam	Density/ $\text{kg}\cdot\text{m}^{-3}$	Compressive strength/Mpa	Hardness/HC	$T_g/^\circ\text{C}$	$T_{5\%}/^\circ\text{C}$	$R_w/\%$
PIF-6	120.12	0.57	81.63	294.90	452.32	60.81
PIF-7	118.40	0.66	81.52	297.81	402.44	55.82
PIF-8	117.61	1.31	88.45	300.32	391.86	56.64
PIF-9	116.23	0.69	81.41	304.64	387.67	53.22
PIF-10	65.72	0.25	60.50	315.65	368.98	52.80

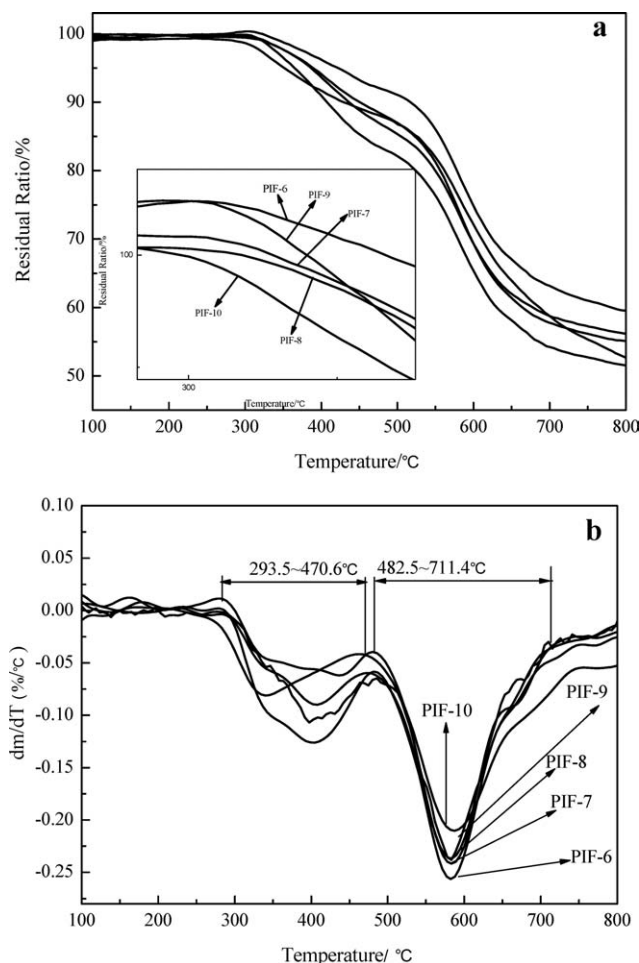


Figure 12. TGA (a) and DTG (b) curves of rigid PI foams with different isocyanate indexes.

CONCLUSIONS

In this article, rigid PI foams were prepared by the reaction of the isocyanate terminated PI prepolymers and deionized water. Chemical structures of rigid PI foams were confirmed by FTIR spectra and the cell was uniform and closed as shown in SEM image. The relationships between water content, isocyanate index and properties of rigid PI foams, including the compressive strength, hardness, density, cell morphology, and thermal

properties, were discussed. The apparent density, hardness, compressive strength, and the $T_{5\%}$ value decreased with the increase of water content. The apparent density and $T_{5\%}$ value decrease whereas the T_g value increase and the hardness, compressive strength first increased and then decreased with the increase of isocyanate index. The rigid PI foams presented excellent thermal stability with the $T_{5\%}$ values were all above 360°C and the R_w value were more than 50% at 800°C.

REFERENCES

- Fay, R. M.; Wulliman, R. S.; Stacy, J. W.; Townsend, J. C. US Pat. 6,565,040, **2003**.
- Weiser, E. S.; Johnson, T. F.; St. Clair, T. L.; Echigo, Y.; Kaneshiro, H.; Grimsley, B. W. *High Perform. Polym.* **2000**, *12*, 1.
- Seibert, H. F. *Reinforced plastic.* **2006**, *1*, 44.
- Wang, L. C.; Guo, B. H.; Zeng, X. M. *Eng. Plastic. Appl.* **2008**, *366*, 8.
- Zhan, M. S.; Wang, K. Nation defense industry press, **2010**.
- Hshieh, F. Y.; Hirsch, H. B.; Beeson, H. D. *Fire Mater.* **2003**, *27*, 119.
- Williams, M. K.; Holland, D. B.; Melendez, O.; Weiser, E. S.; Brenner, J. R. *Polym. Degrad. Stab.* **2005**, *88*, 20.
- Shen, Y. X.; Zhan, M. S.; Wang, K. *Polym. Adv. Technol.* **2010**, *21*, 704.
- Maier, L.; Hu, P.; Seibert, H. *J. Mater. Eng.* **2006**, *37*, 40.
- Seibert, H.; GmbH, R. *Reinforced plastic.* **2000**, *44*, 36.
- Geyer, W.; Seibert, H. US Pat. 5,928,459, **1999**.
- Krieg, M.; Geyer, W. US Pat. 5,698,605, **1997**.
- Riccitiello, S. R.; Sawko, P. M.; Estrella, C. A. US Pat. 4,177,333, **1979**.
- Frey, H. E. US Pat. 3,300,420, **1967**.
- Frosch, R. A. US Pat. 4,184,021, **1980**.
- Rosser, R. W.; Calif, S. J.; Claypool, C. J. US Pat. 3,772,216, **1973**.
- Lee, K. W. US Pat. 4,824,874, **1989**.
- Vazquez, J. M.; Cano, R. J.; Jensen, B. J.; Weiser, E. S. US Pat. 7,541,388, **2009**.
- Liu, X. Y.; Zhan, M. S. *J. Appl. Polym. Sci.* **2010**, *23*, 677.