

## Structures and Properties of Closed-Cell Polyimide Rigid Foams

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**ABSTRACT:** Closed-cell polyimide rigid foams with different Calculated Molecular Weight (Calc'd  $M_n$ ) and foam density ( $\rho$ ) have been prepared by thermal foaming of nadimide-encapped imideoligomers (NAIO) powder. The NAIO powder was obtained by thermally treating of a PMR poly(amide ester) solution derived from the reaction of diethyl ester of 2,3,3',4'-biphenyltetracarboxylic dianhydride ( $\alpha$ -BPDE) and *p*-phenylenediamine (*p*-PDA) using monoethyl ester of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid (NE) as reactive endcapping agent in ethyl alcohol. Effect of Calc'd  $M_n$  and foam density ( $\rho$ ) on mechanical and thermal properties of the polyimide rigid foams have been systematically investigated. It was found that the thermal foaming properties of NAIO powders were affected by the Calc'd  $M_n$ . The appreciate Calc'd  $M_n$  could yield polyimide foams with both high closed-cell content ( $C_c$ ) (>80%) and outstanding mechanical properties. Moreover, the thermal properties were reduced by increasing of Calc'd  $M_n$  and the mechanical properties improved gradually by increasing foam densities. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3282–3291, 2013

**KEYWORDS:** polyimides; foams; mechanical properties

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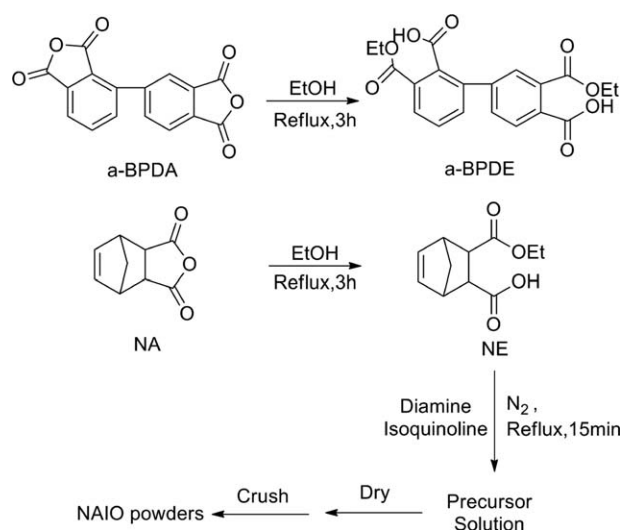
### INTRODUCTION

Polyimide foams, due to their ultra-low weight, excellent thermal insulating and acoustic absorbing properties, high strength-to-weight ratio and cost effectiveness, etc., have been extensively used in many high-tech fields such as aerospace and aviation industries. Polyimide foams are usually employed as thermal and acoustic insulation materials, low dielectric constant materials, as well as structural support materials.<sup>1–5</sup> Currently, there are several commercial polyimide foams, which are partly opened-cell in cellular structures with low  $C_c$  (<42%).<sup>6–12</sup> In 2002, Weiser et al. at NASA Langley Research Center reported that high  $C_c$  (~78%) polyimide foam with  $\rho = 48 \text{ kg m}^{-3}$  was prepared by using intermediate precursor termed "friable balloons".<sup>13,14</sup> However, the  $C_c$  of the foams was obviously reduced with the changes of foam density. For instance, the foams with density of  $96 \text{ kg m}^{-3}$  showed  $C_c$  of only ~42%. Dutruch et al. reported a chemical approach to prepare the polyimide rigid foams by thermal foaming of the nadimide endcapped oligobenzhydrolimides with Calc'd  $M_n$  of  $1000 \text{ g mol}^{-1}$  and  $1500 \text{ g mol}^{-1}$ , respectively.<sup>15</sup> However, the foams prepared from the neat oligomers were too brittle to prepare the testing samples. Hence, polyimide foams must be toughened by blending of thermoplastic polymers.

Chu et al. first reported a method to prepare the thermal cross-linked polyimide foams using 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-ODA as monomers and 2,4,6-triaminopyrimidine (TAP) as crosslinking agent via a poly(ester-amine salt) precursor process. The resulted cross-linked polyimide foams are opened-cell in structures and showed enhanced mechanical strength and modulus.<sup>5,16</sup>

Some patents and articles had also reported another method to prepare polyimide foams with improved mechanical properties.<sup>17–20</sup> These rigid polyimide foams were prepared by reaction of dianhydrides and isocyanates which could generate carbon dioxide as blowing agent. However, the glass transition temperature ( $T_g$ ) of the foams were relatively low (<315°C).<sup>21</sup>

To satisfy the requirements from aerospace and aviation industries for closed-cell polyimide foams with high thermal stability and high compression properties for structural support material applications. A novel chemical pathway has been developed in this laboratory to prepare closed-cell polyimide rigid foams using NAIOs with controlled Calc'd  $M_n$ . The polyimide rigid foams prepared showed high  $C_c$  (>80%) and outstanding thermal properties ( $T_g > 360^\circ\text{C}$ ), being desirable for uses as structural support foam materials. In this study, effect of Calc'd  $M_n$  and foam density on mechanical and thermal properties of the



Scheme 1. Synthetic route of nadimide-encapped imideoligomers.

closed-cell polyimide foams have been systematically investigated.

## EXPERIMENTAL

### Materials

2,3,3',4'-Biphenyltetracarboxylic dianhydride ( $\alpha$ -BPDA), *p*-phenylenediamine (*p*-PDA) and *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid (NA) were purchased from POME Sci-tech, China, and was dried by vacuum oven prior to use. Ethyl alcohol was purchased from Beijing Chemical Reagents Co. and stored over 4 Å molecular sieves prior to use. Isoquinoline was purchased from J&K Co. and used as received.

### Preparation of Nadimide-Encappedimideoligomers

The synthetic route of nadimide-encapped imideoligomers has been shown in Scheme 1.  $\alpha$ -BPDE solution was prepared by refluxing  $\alpha$ -BPDA (45.31 g, 0.154 mol) in dry ethanol (56.67 g, 1.232 mol) for 3 h. NE solution was synthesized by refluxing NA (32.89 g, 0.200 mol) in ethanol (36.80 g, 0.800 mol) for 3 h. *p*-PDA (27.47 g, 0.254 mol) and isoquinoline (0.194 g, 0.0015 mol) were added into the mixture of  $\alpha$ -BPDE and NE solution, and then refluxed with a mechanical stirrer for 15 min in nitrogen atmosphere to get a homogeneous solution. After removed most of the ethanol by rotating distillation, the resulted viscous liquid was dried by baking in a vacuum oven at temperature of  $<200^\circ\text{C}$  to give a solid, which was then crushed and sieved with a mesh to produce the NAI0 powder with Calc'd  $M_n = 1000 \text{ g mol}^{-1}$  (PI-1000).

A series of NAI0 powder with different Calc'd  $M_n$  of  $1500 \text{ g mol}^{-1}$  (PI-1500),  $2000 \text{ g mol}^{-1}$  (PI-2000),  $2500 \text{ g mol}^{-1}$  (PI-2500),  $3000 \text{ g mol}^{-1}$  (PI-3000) have been prepared by the same procedure as PI-1000 by adjusting the mole ratios of  $\alpha$ -BPDA/*p*-PDA according to the reactant mole ratios of NE: $\alpha$ -BPDE:*p*-PDA = 2.00: $n$ :( $n+1$ ).

NAIOs with other aromatic diamines including 3,4'-oxydianiline (3,4'-ODA), 4,4'-oxydianiline (4,4'-ODA), diaminodiphenyl

methane (MDA) or diaminodiphenyl-sulfone (4,4'-DDS) have also been prepared by the similar method as described above.

### Preparation of Closed-Cell Polyimide Rigid Foams

The polyimide rigid foams were prepared by thermal foaming of NAI0 powder in a closed mold. Thus NAI0 powder (PI-1000, PI-1500, PI-2000, PI-2500, or PI-3000) was placed on the bottom of the mold at room temperature, which was then heated in a hot press. After the mold was heated stepwise to  $300\text{--}330^\circ\text{C}$  and held for 3 h, the mold was cooled down to room temperature. The resulted polyimide rigid foam was removed from the mold and cut into the designed size dimensions for testing. The amount of NAI0 powder placed in the mold was determined by the designed foam density and the mold volume as well as the calculated amounts of organic volatiles evolved in the thermal foaming process. Hence, a series of polyimide rigid foams (PIF-1000, PIF-1500, PIF-2000, PIF-2500, and PIF-3000) with different Calc'd  $M_n$  and  $\rho = 100 \text{ kg m}^{-3}$  were prepared.

Similarly, a series of polyimide rigid foams with same Calc'd  $M_n = 1500 \text{ g mol}^{-1}$  but different densities ( $\rho = 50\text{--}400 \text{ kg m}^{-3}$ ) PIF-15-50 ( $\rho = 50 \text{ kg m}^{-3}$ ), PIF-15-100 ( $\rho = 100 \text{ kg m}^{-3}$ ), PIF-15-150 ( $\rho = 150 \text{ kg m}^{-3}$ ), PIF-15-200 ( $\rho = 200 \text{ kg m}^{-3}$ ), PIF-15-300 ( $\rho = 300 \text{ kg m}^{-3}$ ), and PIF-15-400 ( $\rho = 400 \text{ kg m}^{-3}$ ) were prepared, respectively.

### Measurements

The number average molecular weights ( $\overline{M}_n$ ) and polydispersities ( $\overline{M}_w/\overline{M}_n$ ) were determined by gel permeation chromatography (GPC) on a Waters GPC system equipped with a Waters 1515 HPLC pump, a Waters 2414 differential refractometer, and three Styragel columns of HT-3, HT-4, and HT-5, using dimethyl formamide as the eluent at a flow rate of  $1.0 \text{ mL min}^{-1}$  at  $35^\circ\text{C}$ .

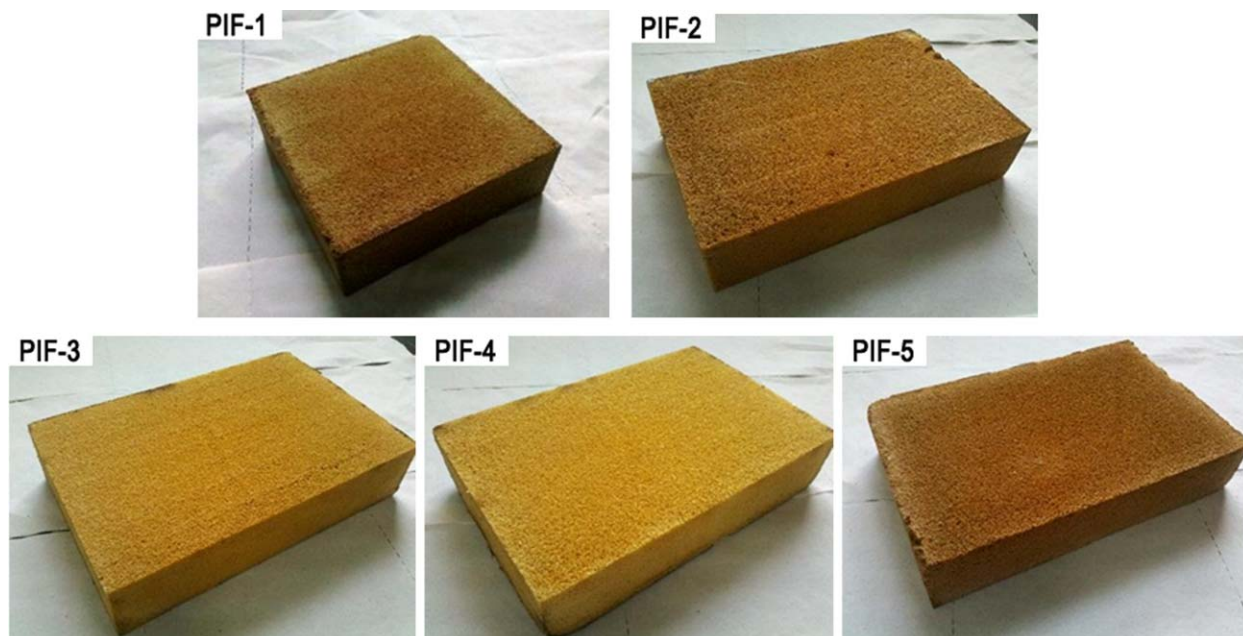
Thermal gravimetric analysis (TGA) was performed on a TA Q50 thermal analysis system at a heating rate of  $20^\circ\text{C min}^{-1}$  in air atmosphere at a flow rate of  $60 \text{ cm}^3 \text{ min}^{-1}$ .

Rheological measurements were carried out on a TA AR2000 rheometer. Specimen disks (20 mm in diameter and 1.5 mm thick) were prepared by compression molding of NAI0 powders at room temperature. The disk was then loaded in the rheometer fixture with 20 mm diameter parallel plates. The top plate was oscillated at a fixed strain of 0.1% and a fixed angular frequency of  $10 \text{ rad s}^{-1}$  while the lower plate was attached to a transducer to record the resulting torque.

Dynamic mechanical analysis (DMA) was performed on a TA Q800 thermal analysis system with a heating rate of  $5^\circ\text{C min}^{-1}$  and a frequency of 1 Hz. A dual cantilever mode was employed with the specimens size  $60.0 \text{ mm} \times 15.0 \text{ mm} \times 5.0 \text{ mm}$ . The storage modulus ( $E'$ ), loss modulus ( $E''$ ) and tangent of loss angle ( $\tan\delta$ ) were recorded as the function of scanning temperature.

Thermal mechanical analysis (TMA) was carried out using a TA Q400 thermal analysis system. The samples were scanned from 20 to  $400^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  under a force of 20 mN.

Mechanical properties of the polyimide rigid foams were measured on an Instron 5567 universal testing machine.



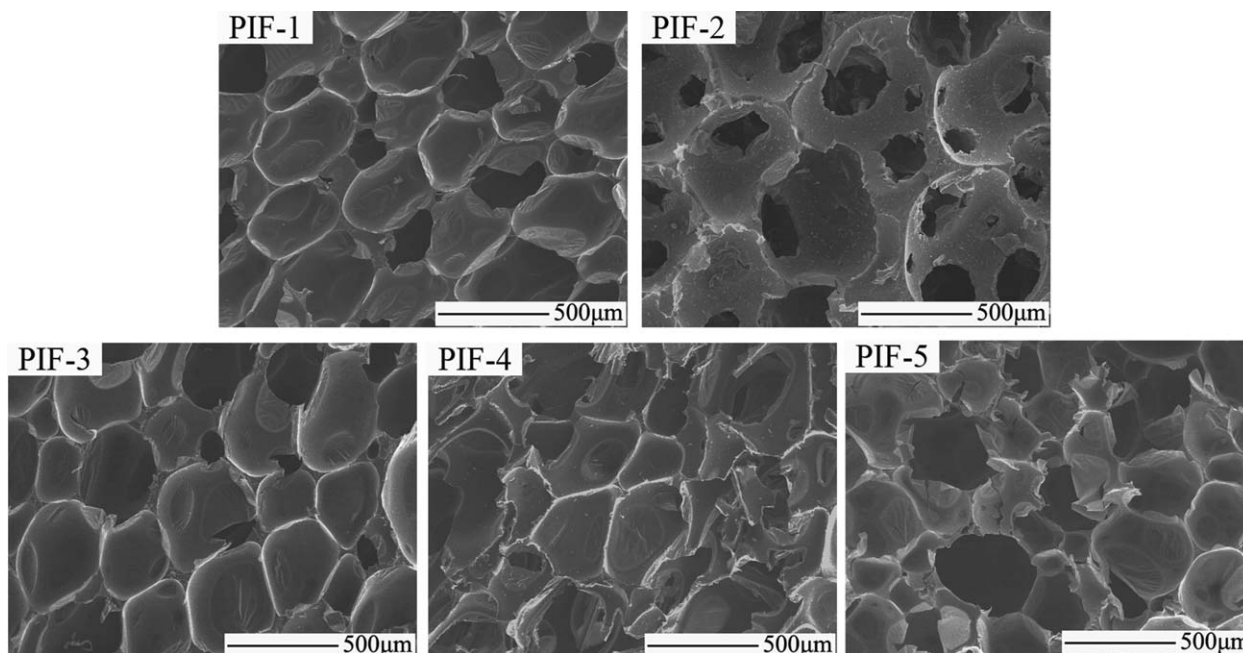
**Figure 1.** Thermal foaming of NAIOS with different aromatic dianamines. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Compression strength ( $c_c$ ) and modulus ( $c_m$ ) of foams were obtained by using specimens cut into 25.0 mm  $\times$  25.0 mm  $\times$  25.0 mm at a compression rate of 2.5 mm min<sup>-1</sup>. Tensile strength ( $\sigma_b$ ) and modulus ( $\sigma_m$ ) were measured according to GB/T 9641-88, with dumbbell-shape specimens at a tensile rate of 5 mm min<sup>-1</sup>. Flexural strength ( $f_s$ ) and modulus ( $f_m$ ) of foams were obtained using 25.0 mm wide and 20.0 mm thick specimens with a span of 100.0 mm at a rate of 10.0 mm min<sup>-1</sup> in accordance with GB/T 8812.1-2007. Compression creep test were

conducted by using specimens cut into 25.0 mm  $\times$  25.0 mm  $\times$  25.0 mm at a compression rate of 2.5 mm min<sup>-1</sup>.

Cellular structure morphology of foams was observed by scanning electron microscopy (SEM, Hitachi S4300).

Closed-cell content measurements were performed on Micromeritics Accucyc II 1340 according to GB/T 10799-2008 using specimen with the size of 25.0 mm  $\times$  25.0 mm  $\times$  25.0 mm under a pressure of 2.9 psi.



**Figure 2.** SEM photographs of the polyimide rigid foams derived from different aromatic dianamines.



**Table I.** Thermal Foaming Results of 3,4'-ODA-Based NAIOS with Different Dianhydrides and Endcapping Agents

Endcap Dianhydride	NA	3-APA	PEPA
$\alpha$ -BPDA	Uniform, Closed-cell	Collapsed	Collapsed seriously
ODPA	Collapsed	Collapsed seriously	Collapsed completely
BTDA	Non-uniform	Collapsed seriously	Collapsed completely
PMDA	Non-uniform	Collapsed seriously,	Collapsed completely,

## RESULTS AND DISCUSSION

### Thermal Foaming Properties of NAIOS with Different Chemical Structures

A novel chemical pathway to prepare closed-cell polyimide rigid foams has been reported in this laboratory by thermal foaming of NAIOS powders at temperature of 300–330°C. The NAIOS were synthesized by reacting of  $\alpha$ -BPDE and aromatic diamines including *p*-PDA (PI-1), 3,4'-ODA (PI-2), 4,4'-ODA (PI-3), MDA (PI-4) or 4,4'-DDS (PI-5) using NE as reactive endcapping agent. It was found that the NAIOS thermal foaming properties was attributed to the blowing of cyclopentadiene (CPD) which was evolved from thermal decomposition of the nadimide endcapps in the imideoligomer by the reverse Diels-Alder reaction during crosslinking of the bisnadimide oligomers.<sup>12</sup> Figures 1 and 2 compare the thermal foaming results of different NAIOS. It can be seen that all of the NAIOS could produce high quality polyimide rigid foams with uniform cellular structures. However, if  $\alpha$ -BPDA in PI-2 ( $\alpha$ -BPDA/3,4'-ODA/NA) was replaced by other dianhydride (4,4'-oxydiphthalic anhydride (ODPA) for example) to give a new NAIOS (ODPA/3,4'-ODA/NA) or NA replaced by other endcaps such as 3-ethynylaniline (3-APA) or 4-Phenylethynylphthalic anhydride (PEPA) to give NAIOS ( $\alpha$ -BPDA/3,4'-ODA/3-APA, or  $\alpha$ -BPDA/3,4'-ODA/PEPA) the NAIOS could lead to collapsed or nonuniformed cellular structures (Table I), implying that the rigid and asymmetrical molecule structure of  $\alpha$ -BPDA could not only improve foaming capability as the asymmetrical structure increase the “free volume” among molecule chains which could act as the initial foaming point, but also rise the  $T_g$  of polymer matrix to endure the high curing temperature of NA which decomposed CPD as blowing agent that the other two crosslinking agent cannot generate.

### Effect of Calc'd $M_n$ on NAIOS Thermal Foaming Properties

On the basis of the observations as described above, NAIOS ( $\alpha$ -BPDA/*p*-PDA/NA) has been selected to investigate the effect of Calc'd  $M_n$  on the mechanical and thermal properties of the polyimide rigid foams. Thus, a series of NAIOS powders with different controlled Calc'd  $M_n$  have been prepared. The molecule weights of these NAIOS powders determined by GPC are summarized in Table II. The  $\overline{M}_n$  of the oligomers determined by GPC were accordance with the trend of the designed molecular weight but a little greater than the calculated ones with polydispersities of 1.48–2.16. The thermal foaming properties of NAIOS powders have been changed by either increasing or decreasing of Calc'd  $M_n$  (Figure 3). It can be seen that NAIOS powders with Calc'd  $M_n = 1000$  to 2500 g mol<sup>-1</sup> (PI-1000, PI-1500, PI-2000, and PI-2500) could be easily thermal foaming to

give homogeneous polyimide foams. However, PI-3000 could be only partly foamed. It also can be seen from Figure 4 that the pore of foams became smaller and less uniform, due to decreasing amount of blowing agent CPD with Calc'd  $M_n$  increasing. Figure 5 compares the rheological behaviors of NAIOS powders with different Calc'd  $M_n$ . It can be seen that the NAIOS minimum melt viscosities were increased gradually with increasing of Calc'd  $M_n$ , i.e., 78 Pa s at 254°C for PI-1000, 144 Pa s at 280°C for PI-1500, and 1280 Pa s at 279°C for PI-2500, respectively. PI-3000 showed melt viscosity of as high as 2374Pa·s at 306°C, much higher than others, resulting in poor thermal-foaming performance, probably due to the insufficient amount of blowing agent (CPD), and low melt flowability.

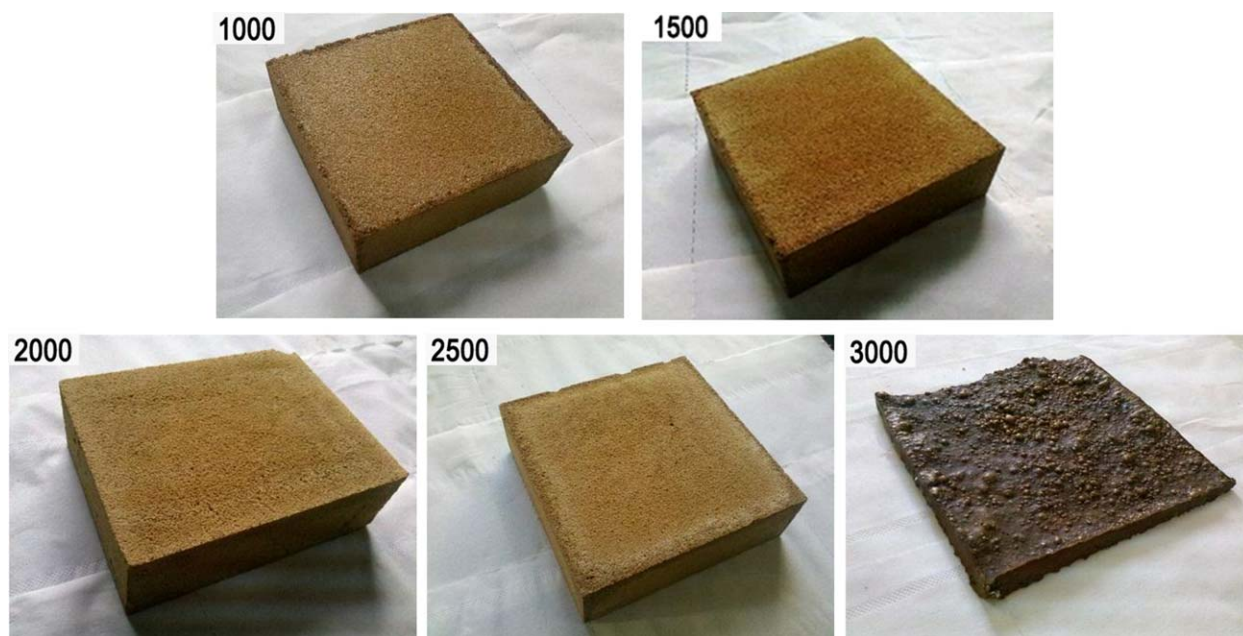
### Closed-Cell Percent and Thermal Properties of Polyimide Rigid Foams

Figure 6 compares the closed-cell percent ( $C_c$ ) of the polyimide rigid foams with different Calc'd  $M_n$ . PIF-2000 showed the highest  $C_c$  of 92%, compared to 85% for PIF-1000, 88% for PIF-1500, and 86% for PIF-2500, respectively. The  $C_c$  of polyimide foams was controlled by factors such as melt viscosity, melt strength, and amount of blowing agent etc. The melt viscosity would determine the thermal-foaming ability of the melt resins and the melt strength and toughness were critical factors on whether opened- or closed-cell structures could be produced. The concentration of blowing agent was also a key factor to produce closed-cell structure. PIF-1000 has the lowest melt viscosity due to its lowest Calc'd  $M_n$ , meanwhile, its melt strength and toughness are relative poor than PIF-1500 and PIF-2000 due to the short polyimide backbone chains, resulted in the polyimide foams with opened cell structures.

Table III summarizes the thermal properties of the polyimide rigid foams. Temperature at 5% loss of original weight ( $T_5$ ) of 468–491°C and temperature at 10% loss of original weight ( $T_{10}$ ) of 506–565°C could be observed respectively. Moreover, no any of weight loss was detected before the temperature

**Table II.** Molecular Weight of the NAIOS Powders with Different Calc'd  $M_n$ 

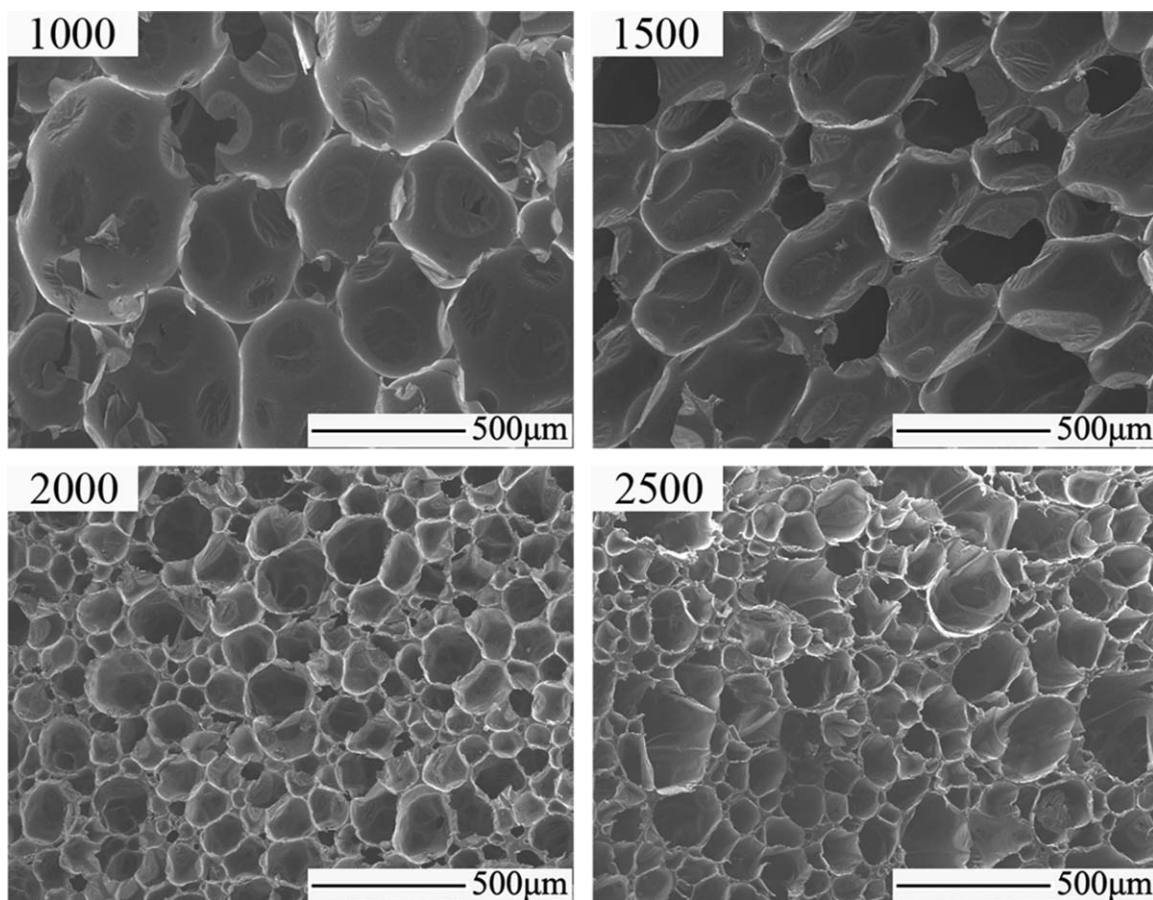
Samples	Calc'd $M_n$	$\overline{M}_n$ (g·mol <sup>-1</sup> )	$\overline{M}_n$ (g·mol <sup>-1</sup> )	$\overline{M}_w/\overline{M}_n$
PI-1000	1000	2393	4071	2.16
PI-1500	1500	2686	4125	1.48
PI-2000	2000	3435	5692	1.56
PI-2500	2500	4093	7030	1.63
PI-3000	3000	3996	6627	1.59



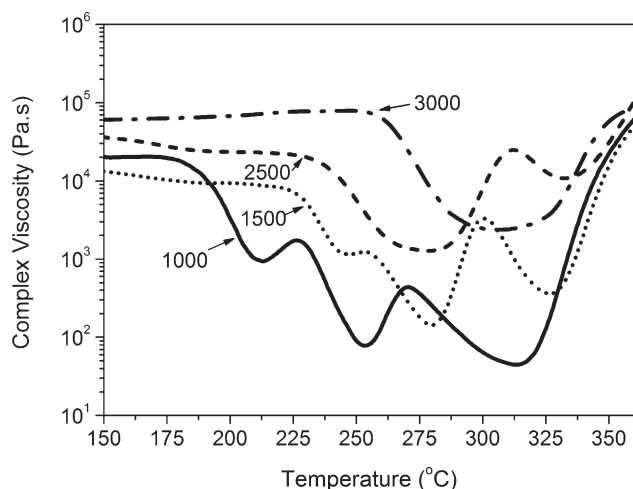
**Figure 3.** Thermal foaming results of NAIOs with different Calc'd  $M_n$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

scanned to 350°C in TGA (Figure 7). The  $T_g$  determined by  $\tan\delta$  in DMA were measured in the range of 361 to 389°C, which was reduced with rising of Calc'd  $M_n$ . For instance,

PIF-1000 has  $T_g$  of 389°C, compared with 374°C for PIF-1500, 361°C for PIF-2000 and 365°C for PIF-2500, respectively. The coefficient of thermal expansion (CTE) of the polyimide rigid



**Figure 4.** SEM photographs of the polyimide rigid foams derived from different Calc'd  $M_n$ .



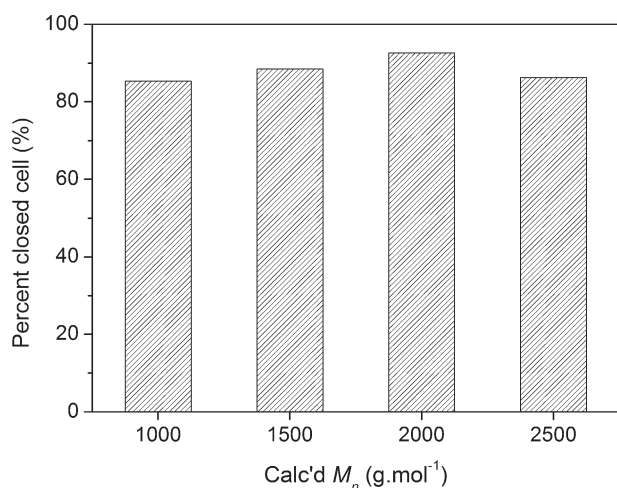
**Figure 5.** Rheological behaviors of NAI0 powders with different Calc'd  $M_n$ .

foams was measured in the range of  $40\text{--}43 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  at  $30\text{--}300^\circ\text{C}$ .

### Mechanical Properties of the Polyimide Rigid Foams

Table IV summarizes the mechanical properties of the polyimide rigid foams. The flexural modulus ( $f_m$ ) decreased from 28.2 MPa for PIF-1000, to 20.1 MPa for PIF-1500, 18.7 MPa for PIF-2000 and 6.4 MPa for PIF-2500, respectively. The flexural strength ( $f_s$ ) also reduced with rising of Calc'd  $M_n$ . The tensile strength ( $\sigma_b$ ) was measured in the range of 0.44–0.96 MPa and tensile modulus ( $\sigma_m$ ) of 7.23–27.4 MPa, respectively. The elongations at breakage ( $\varepsilon$ ) was ranged at 4.3–4.9% for the polyimide foams with Calc'd  $M_n = 1000\text{--}2000 \text{ g mol}^{-1}$ , which reached to 9.0% for PIF-2500, indicating that the polyimide rigid foams have good toughness. In comparison, PIF-1500 showed the best combination of mechanical properties with  $f_m = 20.1 \text{ MPa}$ ,  $f_s = 1.19 \text{ MPa}$ ,  $\sigma_b = 0.96 \text{ MPa}$ , and  $\varepsilon = 4.6\%$ , respectively.

Table V shows the compression properties of the polyimide rigid foams both at room temperature and elevated



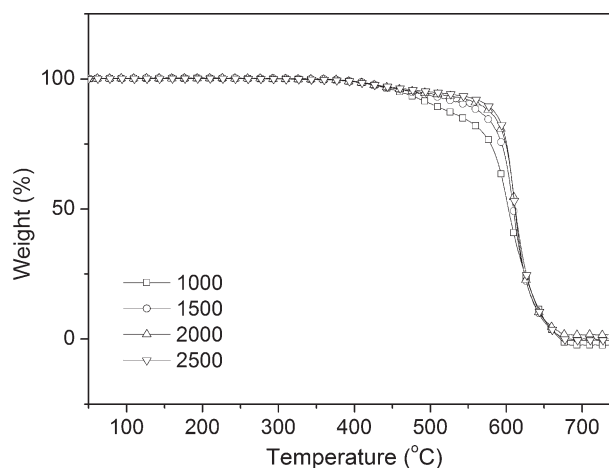
**Figure 6.**  $C_c$  of the polyimide rigid foams with different Calc'd  $M_n$ .

**Table III.** Thermal Properties of the Polyimide Rigid Foams with Different Calc'd  $M_n$

Calc'd $M_n$ ( $\text{g mol}^{-1}$ )	TGA		DMA		TMA
	$T_5$ ( $^\circ\text{C}$ )	$T_{10}$ ( $^\circ\text{C}$ )	$E'$ ( $^\circ\text{C}$ )	$\tan \delta$ ( $^\circ\text{C}$ )	CTE ( $10^{-6} \text{ } ^\circ\text{C}^{-1}$ ) <sup>a</sup>
1000	468	506	361	389	41
1500	491	558	345	374	42
2000	475	560	337	361	43
2500	480	565	334	365	40

<sup>a</sup>CTE was determined at  $30\text{--}300^\circ\text{C}$ .

temperatures. In general, polyimide foams with low molecule weight, crosslinking points densities of which were much more higher, had better compression properties as the crosslinking network could confine the movability of molecule chain and made the foams much stiffer (PIF-1500>PIF-2000>PIF-2500). However, increasing of the crosslinking points could not only increase the stiffness of foams, but also increase the fragility which could strongly affect the properties. As a result, PIF-1000 showed inferior compression properties comparing to PIF-1500. PIF-1500 which reach to a balance of the stiffness and fragility showed the best compression properties at room temperature ( $c_m = 37.1 \text{ MPa}$  and  $c_s = 1.34 \text{ MPa}$ ), compared with PIF-1000 ( $c_m = 29.0 \text{ MPa}$  and  $c_s = 1.24 \text{ MPa}$ ) and PIF-2500 ( $c_m = 22.7 \text{ MPa}$  and  $c_s = 0.89 \text{ MPa}$ ), respectively. At  $300^\circ\text{C}$ , the compression properties were reduced by  $\sim 48\%$  for modulus and  $\sim 52\%$  for strength. For instance, PIF-1500 has  $c_m = 37.1 \text{ MPa}$  and  $f_s = 1.34 \text{ MPa}$  at room temperature, which was reduced to 22.5 MPa (61%) and 0.71 MPa (53%) at  $300^\circ\text{C}$ , respectively, higher than the others either. The polyimide rigid foams also showed excellent compression creep properties (0.18–0.23%) under 0.4 MPa for 2 h at room temperature. But a quite different phenomenon was shown at  $250^\circ\text{C}$ , PIF-1500, and PIF-1000 still exhibited very low compression creeps (1.03% and 1.28%, respectively) as the crosslinking networks could stabilize the molecule chain to ensure the structural integrity of foams at



**Figure 7.** TGA curve of the polyimide rigid foams with different Calc'd  $M_n$ .



**Table IV.** Mechanical Properties of the Polyimide Rigid Foams with Different Calc'd  $M_n$ 

Calc'd $M_n$ (g mol <sup>-1</sup> )	Tensile properties			Flexural properties	
	$\sigma_m$ (MPa)	$\sigma_b$ (MPa)	$\varepsilon$ (%)	$f_m$ (MPa)	$f_s$ (MPa)
1000	18.6 ± 2.2	0.62 ± 0.09	4.3 ± 0.7	28.2 ± 4.8	1.36 ± 0.19
1500	27.4 ± 2.6	0.96 ± 0.08	4.6 ± 0.5	20.1 ± 4.2	1.19 ± 0.20
2000	18.5 ± 1.4	0.75 ± 0.04	4.9 ± 0.6	18.7 ± 3.18	1.17 ± 0.19
2500	7.23 ± 0.9	0.44 ± 0.06	9.0 ± 1.4	6.4 ± 1.10	0.59 ± 0.07

**Table V.** Compression Properties of the Polyimide Rigid Foams with Different Calc'd  $M_n$ 

Calc'd $M_n$ (g mol <sup>-1</sup> )	$c_m$ (MPa)		$c_s$ (MPa) at 10% deformation		Compression creep <sup>a</sup> (%)	
	RT	300	RT	300	RT	250
1000	29.0 ± 2.1	17.5 ± 1.1	1.24 ± 0.06	0.70 ± 0.02	0.18	1.28
1500	37.1 ± 7.1	22.5 ± 1.3	1.34 ± 0.23	0.71 ± 0.02	0.18	1.03
2000	32.0 ± 9.7	20.6 ± 2.3	1.27 ± 0.08	0.61 ± 0.02	0.23	3.87
2500	22.7 ± 1.9	11.9 ± 4.6	0.89 ± 0.05	0.50 ± 0.04	0.22	10.31

<sup>a</sup>Creep test was conducted under 0.4 MPa for 2 h.

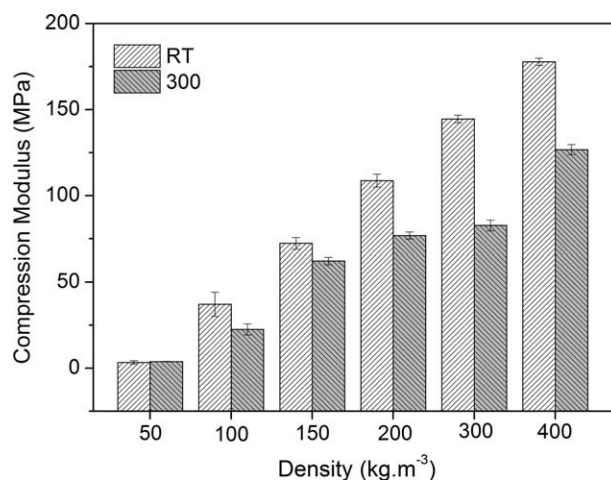
high temperature. However, the polyimide foams with higher Calc'd  $M_n$  (PIF-2000 and PIF-2500) which were lack of enough crosslinking points, showed increased compression creeps (3.87% for PIF-2000 and 10.3% for PIF-2500, respectively).

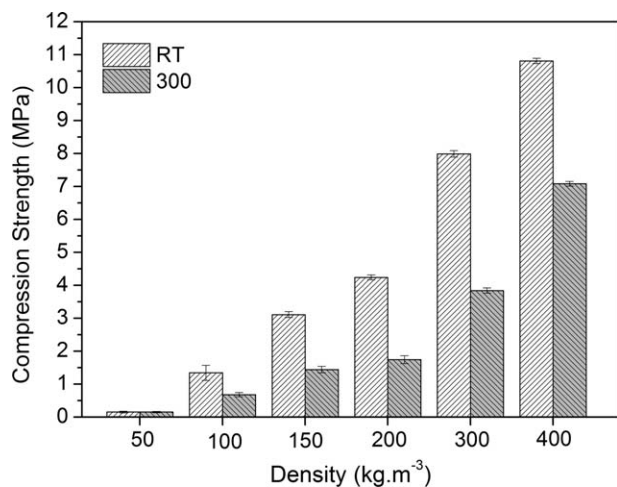
#### Mechanical Properties of Polyimide Foams with Different Density

Density of these foams can range from 50 kg m<sup>-3</sup> to 400 kg m<sup>-3</sup>. Making subtle changes in chemistry, density and open or closed cell content, the physical properties of foams can be tuned to an application. It has been shown experimentally and theoretically that density is the most important parameter affecting physical properties.<sup>22,23</sup> As exhibited in the foregoing paragraphs, PIF-1500 showed the most excellent properties (relatively high  $T_g$ , tensile and flexural property, the highest class of compression properties) comparing with the other polyimide foams with different Calc'd  $M_n$  and same density of 100 kg m<sup>-3</sup>, we choose NAI0 powder with Calc'd  $M_n$  of 1500 g mol<sup>-1</sup> to prepare foams with different densities and illustrate how density affect the mechanical properties and closed-cell content of the rigid polyimide foams.

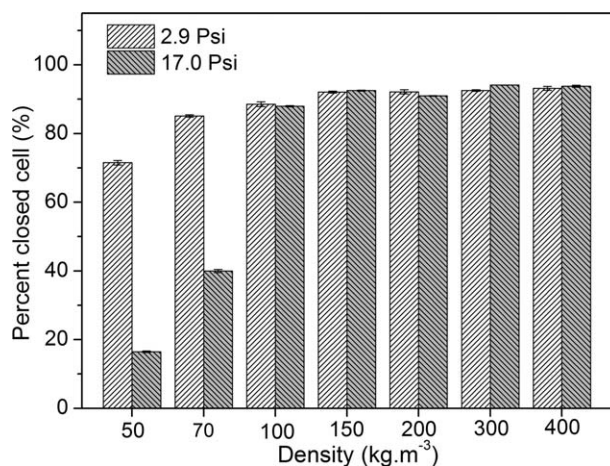
Figure 8 depicts the dependence of the  $c_m$  of the polyimide foams on its densities ( $\rho$ ) both at room temperature and 300°C. It can be seen that  $c_m$  of the polyimide rigid foams at room temperature increased gradually with  $\rho$  increasing. At  $\rho < 100$  kg m<sup>-3</sup>,  $c_m$  increased from 3.3 MPa at  $\rho = 50$  kg m<sup>-3</sup> to 37.1 MPa at  $\rho = 100$  kg m<sup>-3</sup>, then which was increased obviously from 37.1 MPa at  $\rho = 100$  kg m<sup>-3</sup> to 72.3 MPa at  $\rho = 150$  kg m<sup>-3</sup> and 108.7 MPa at  $\rho = 200$  kg m<sup>-3</sup>, respectively. The polyimide foams with  $\rho = 300$  kg m<sup>-3</sup> and 400 kg m<sup>-3</sup> showed  $c_m$  of as high as 144.5 MPa and 177.8 MPa, respectively. It was noteworthy that the polyimide foams showed

very high modulus retention at 300°C. For instance, the polyimide foams with  $\rho = 400$  kg m<sup>-3</sup> and 100 kg m<sup>-3</sup> showed modulus retention of 60–70%. The  $c_s$  of polyimide foams also showed obvious dependence on its  $\rho$  both at ambient temperature and at 300°C (Figure 9). The  $c_s$  at room temperature for the polyimide foam with  $\rho = 100$  kg m<sup>-3</sup> was measured at 1.3 MPa, increased to 3.1 MPa at  $\rho = 150$  kg m<sup>-3</sup> and 8.0 MPa at  $\rho = 300$  kg m<sup>-3</sup>, respectively, indicating that polyimide foams could be strengthened apparently by increasing its density. At 300°C, the polyimide foams also showed reasonable compression strength. For instance, the polyimide foams with  $\rho = 100$  kg m<sup>-3</sup> and 400 kg m<sup>-3</sup> exhibited strength retention of >50%, demonstrating that the polyimide foams have outstanding thermal stabilities.

**Figure 8.** Compression modulus of the polyimide rigid foams with different densities.



**Figure 9.** Compression strength of the polyimide rigid foams with different densities.

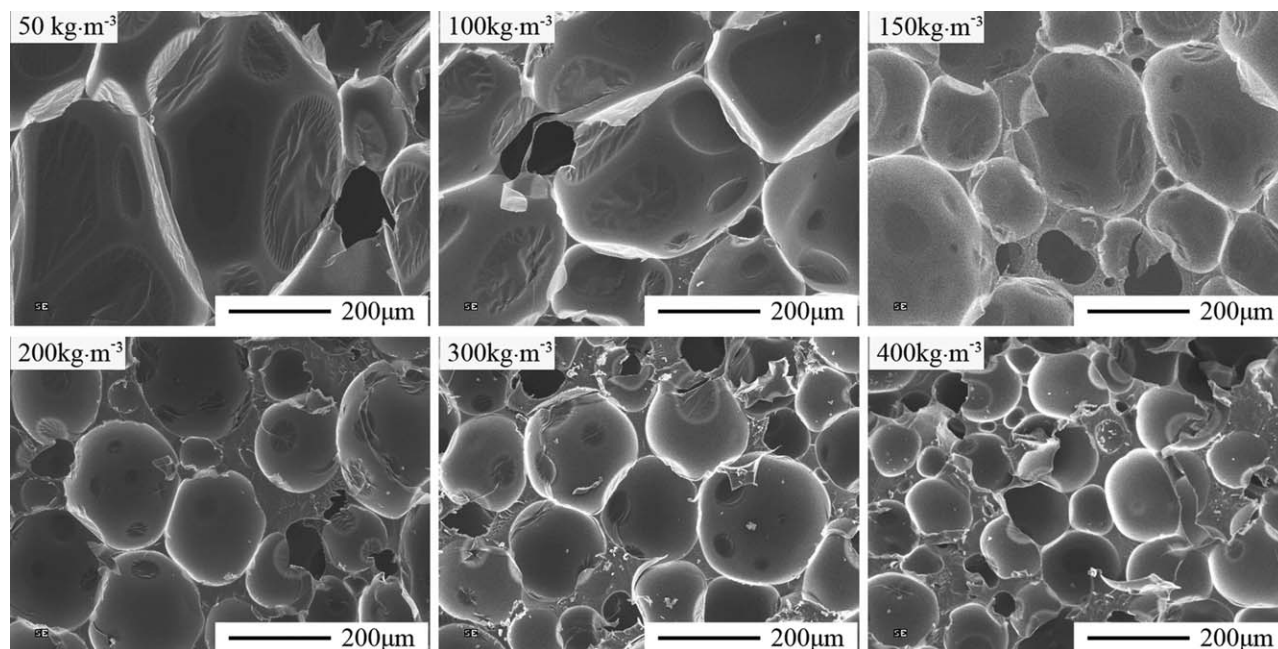


**Figure 10.** Closed-cell percent of the polyimide rigid foams with different densities.

### Closed-Cell Percent and Thermal Properties of Polyimide Foams with Different Densities

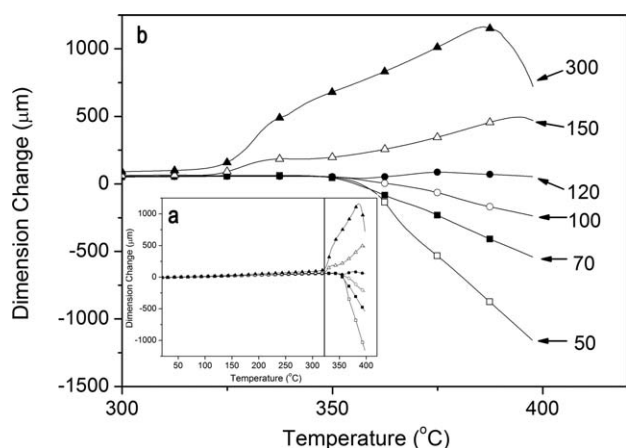
Figure 10 reveals the dependence of the closed-cell percent ( $C_c$ ) on the foam densities at two levels of testing pressures. At a lower testing pressure (2.9 psi),  $C_c$  was measured at 72% for polyimide foam with  $\rho = 50 \text{ kg m}^{-3}$ , then increased gradually to 85% at  $\rho = 70 \text{ kg m}^{-3}$  and finally reached to 89% at  $\rho = 100 \text{ kg m}^{-3}$  with the density increasing. However, at a higher testing pressure of 17.0 psi, much lower  $C_c$  was observed for polyimide foams with lower densities ( $\rho < 100 \text{ kg m}^{-3}$ ). For instance, polyimide foam with  $\rho = 70 \text{ kg m}^{-3}$  showed  $C_c$  of 85% at 2.9 psi and 40% at 17.0 psi, respectively. However,  $C_c$  of  $\sim 90\%$  have been reached for the polyimide foams with higher densities ( $\rho > 100 \text{ kg m}^{-3}$ ) both at 2.9 and 17.0 psi. This indicated that

the low-density polyimide foams have weaker cell in the cellular foam structures, which could be damaged under high testing pressure. Figure 11 compares the SEM photographs of the polyimide foams with different densities. It can be seen that the low-density foam have obvious big size cells. The cell size was about  $600 \mu\text{m}$  for polyimide foam with  $\rho = 50 \text{ kg m}^{-3}$ , then decreased gradually to  $400 \mu\text{m}$  at  $\rho = 100 \text{ kg m}^{-3}$  and  $200 \mu\text{m}$  at  $\rho = 400 \text{ kg m}^{-3}$  with the density increasing. Meanwhile, the thickness of vertices merged by adjacent cell, which bond cells to an integrity and strengthen the foams, increased with the density increasing. Both of small cell size and thick vertices made the high density foams have higher resin content per unit volume, which was the determinative effect on the mechanical properties of the polyimide foams.



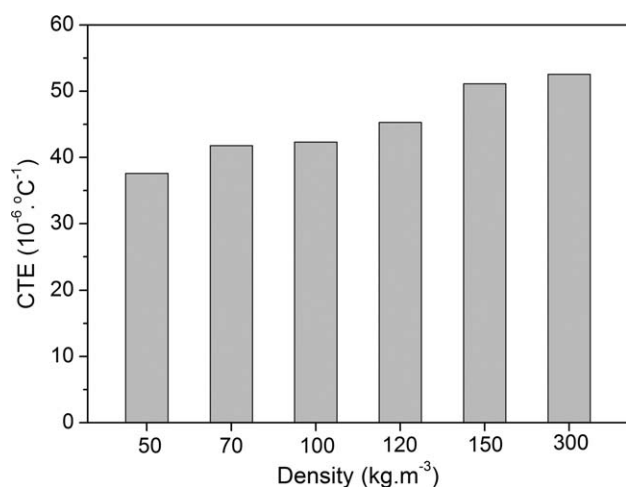
**Figure 11.** SEM photographs of the polyimide rigid foams with different densities.





**Figure 12.** TMA curves of the polyimide rigid foams with different densities.

Figure 12 shows TMA curves of the polyimide foams with different densities. At temperature of  $<320^{\circ}\text{C}$ , the polyimide foams showed linear thermal dimension expansion with increasing of temperatures. The coefficient of thermal expansion (CTE) was measured at about  $38\text{--}53 \times 10^{-6} \cdot ^{\circ}\text{C}^{-1}$  (Figure 13), and polyimide foams with high density had relatively high CTE. Abrupt changes in thermal expansions have been observed at  $>320^{\circ}\text{C}$  [Figure 12(b)]. The polyimide foams with  $\rho < 120 \text{ kg m}^{-3}$  showed dimension shrinkages and that with  $\rho > 120 \text{ kg m}^{-3}$  expanded in dimension with increasing temperatures. This could be interpreted by the loading force (20 mN) on the testing samples, resulted in the foam cell shrinkage at temperature near  $T_g$  for the low-density foams due to its big size and weak cells. The high-density foams with  $\rho > 120 \text{ kg m}^{-3}$  were strong enough to endure the preloading force on the testing samples and exhibited the same thermal expansion behaviors as solid resin without cellular structures. This observation was well accordance with the conclusion derived from the compression property and closed-cell content testing that high-density foams have strong small size cells, resulted in thermal stable and stiffer foams. The density of  $120 \text{ kg m}^{-3}$  was the critical point above



**Figure 13.** CTE of the polyimide rigid foams with different densities.

which foam would have high closed-cell content and excellent mechanical properties.

## CONCLUSIONS

Closed-cell polyimide rigid foams with different Calc'd  $M_n$  and foam densities have been prepared. There are obvious effects of Calc'd  $M_n$  and foam densities on mechanical and thermal properties of the polyimide rigid foams. Generally, low Calc'd  $M_n$  could yield foams with improved  $T_g$ , flexural, and compression properties, but excessively low Calc'd  $M_n$  could also make foams to be fragile and oapp39567ed-cell. Thus, only the appropriate Calc'd  $M_n$  could yield polyimide foams with both high closed-cell percent and outstanding mechanical properties. Moreover, the mechanical properties could be improved gradually by increasing the foam densities which decreased the cell size and meanwhile rose the thickness of the cell vertices. The density of  $120 \text{ kg m}^{-3}$  was the critical point above which foam would have high closed-cell content and excellent mechanical properties.

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