

## Preparation and characterization of highly thermostable polyisocyanurate foams modified with epoxy resin

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**ABSTRACT:** A series of epoxy resin–modified polyisocyanurate (EP-PIR) foams with oxazolidone (OX) rings and isocyanurate (IS) rings have been successfully prepared by the reaction of polymethylene polyphenyl isocyanate (PAPI) and diglycidyl ether of bisphenol-A (DGEBA). Fourier transform infrared spectroscopy and differential scanning calorimetry are performed to investigate the influence of curing temperature on the chemical structure of EP-PIR foams. The results indicate that low temperature is beneficial to the formation of the IS ring, and high temperature is in favor of the OX ring. The influence of the mole ratio of [PAPI]/[DGEBA] on the mechanical properties and thermal stability has also been studied. With the increase of [PAPI]/[DGEBA], the specific compressive strength shows a maximum of  $0.0135 \pm 0.0003$  MPa m<sup>3</sup>/kg. The optimized mole ratio of [PAPI]/[DGEBA] is around 2.5 to reach the better mechanical and thermal properties, and the glass-transition temperature is as high as 323.5°C. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43085.

**KEYWORDS:** foams; mechanical properties; thermal properties

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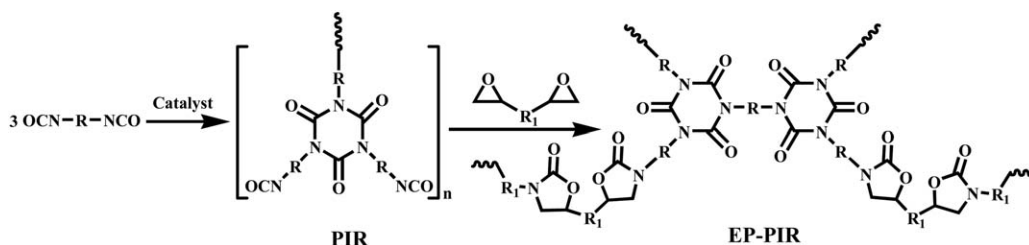
### INTRODUCTION

Polyisocyanurate (PIR) foams are isocyanate-based insulating materials, which are based on the reaction of polycyclotrimerization of diisocyanates or isocyanate-terminated prepolymers. They are widely used in civil engineering and military applications.<sup>1</sup> However, pure PIR foams consist of highly crosslinked six-member isocyanurate rings, which make them extremely brittle. This brittle property of PIR foams has limited their practical application despite their inherently excellent thermal stability and flame resistance.<sup>2</sup>

An effective way to overcome the fragility of PIR foams is to modify them with polyether polyol and polyester polyol, which is attached to isocyanurate rings via urethane groups, to produce polyurethane–polyisocyanurate (PUR–PIR) foams.<sup>3–6</sup> However, the introduction of the flexible polyols results in significant decreases in thermal stability and flame retardance, and the maximum service temperature of PUR–PIR foams is typically below 150°C.<sup>4</sup> A great effort has been made to improve the physicochemical properties of PUR–PIR foams. Boroorganic compounds, borate, aluminum hydroxide, expandable graphite, phosphonates, and zinc salts are used as fillers to improve the thermal and flame retardance of PUR–PIR foam.<sup>7–14</sup> However, a low content of fillers gives rise to limited

improvement of flame retardancy, whereas a high content causes high viscosity and poor mechanical properties.<sup>10</sup>

Another good strategy to overcome the fragility of PIR is to insert heterocyclic rings in the polymer structure, increasing the distance between crosslinking points. Introducing a linear oxazolidone structure to reduce the crosslink density of PIR polymer can enhance the mechanical toughness.<sup>15</sup> Simultaneously, the heterocyclic oxazolidone structure is favorable to improve the thermal stability and flame retardance.<sup>16</sup> As shown in Scheme 1, the linear oxazolidone structure is formed by the reaction of isocyanate and epoxy resin, resulting in epoxy-modified polyisocyanurate polymers, which are also called poly(isocyanurate oxazolidone) resins (PISOX) containing both isocyanurate and oxazolidone groups.<sup>17,18</sup> Kordomenos studied the kinetics of the thermal dissociation of epoxy resin–modified polyisocyanurate (EP-PIR) polymers by dynamic and isothermal thermogravimetric analysis, and the results showed that the thermostability of the groups increased in the following order: urethanes < oxazolidones < isocyanurates.<sup>19</sup> The fraction of oxazolidone and isocyanurate groups present in the final network depends on the initial isocyanate/epoxy ratio and the curing conditions.<sup>20</sup> Chian has investigated the effect of stoichiometry of diglycidyl ether of bisphenol-A (DGEBA) and polymeric diphenyl methane diisocyanate (pMDI) on the molecular



**Scheme 1.** Chemical structure of epoxy-modified polyisocyanurate resin with oxazolidone and isocyanurate groups.

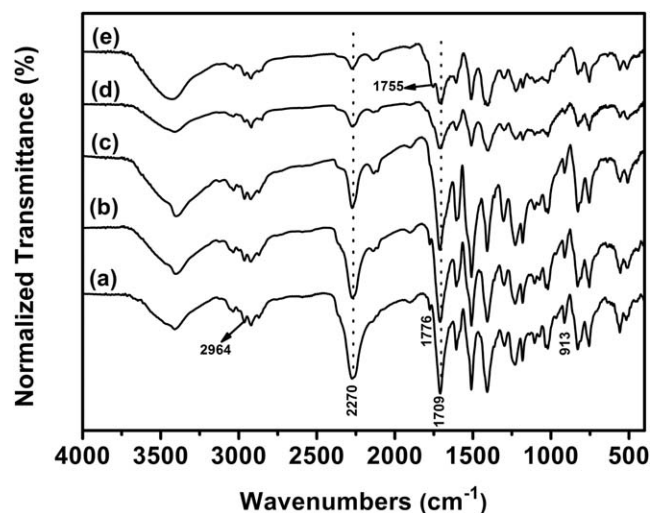
structure and mechanical and thermal properties of EP-PIR polymers.<sup>15</sup> Although many researchers pay attention to the EP-PIR polymers, little attention has been given to the EP-PIR foams with an oxazolidone heterocyclic ring structure.

In the present paper, a series of EP-PIR foams with oxazolidone (OX) rings and isocyanurate (IS) rings were prepared by the reaction of polymethylene polyphenyl isocyanate (PAPI) and DGEBA, and 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) was used as a catalyst. The influence of the curing condition and stoichiometry of [PAPI]/[DGEBA] on the structure, morphology, thermal stability, and mechanical properties of EP-PIR foams was investigated.

## EXPERIMENTAL

### Materials

A low-molecular-weight epoxy resin, diglycidyl ether of bisphenol-A (epoxy value = 0.51) was supplied by the Chenguang plant (Chenguang Research Institute of Chemical Industry, Chengdu, China) and used after drying under vacuum. Polymethylene polyphenyl isocyanate (WANNATE PM-200, NCO % = 31.3%, Wanhua Chemical Reagent Co., Yantai, China), poly-siloxane-polyether copolymer (AK8807, Nanjing Demei Shi Chuang Chemical Co., Nanjing, China) as surfactant, and 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30, Shanghai Chemical Reagent Co., Shanghai, China) as catalyst were used as received.



**Figure 1.** FTIR spectra of EP-PIR foams cured at different temperatures: (a) 75°C for 2 h, (b) 100°C for 2 h, (c) 150°C for 2 h, (d) 180°C for 2 h, and (e) 220°C for 2 h. The mole ratio of [PAPI]/[DGEBA] is 2.5.

### Preparation of the EP-PIR Foam

Briefly, the DGEBA, PAPI, and surfactant were added in a 250-mL glass beaker and mixed by mechanical stirrer at different molar ratios of [PAPI]/[DGEBA] (1, 1.5, 2, 2.5, 3, 4, 5, 6, and 8). The weight percent of AK8807 was 3 wt % based on the total weight of PAPI and DGEBA. Then the catalyst DMP-30 (1 wt %) and blowing agent H<sub>2</sub>O (0.25 wt %) were added into the above mixture and stirred with a high-speed mixer (about 2000 rpm) for 10–45 seconds. The mixture was cast into an aluminum mold and molded foaming at room temperature for 4 h. Then the EP-PIR foam was transferred into an oven and postcured gradually at 75°C, 100°C, 130°C, 150°C, 180°C, and 220°C for 2 h.

### Scanning Electron Microscopy

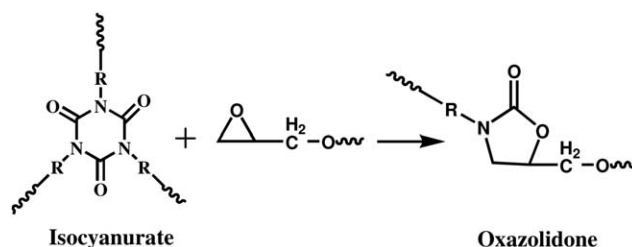
The morphologies of EP-PIR foams were investigated with a CamScan Apollo 300 (Obducat CamScan Ltd., Cambridge, United Kingdom) field emission scanning electron microscope (FE-SEM). For SEM analysis, samples were mounted on aluminum studs using adhesive graphite tape and sputter-coated with gold before analysis. The size distribution of bubbles was calculated by the Image-Pro Plus software (Media Cybernetics, Inc., Bethesda, Maryland).

### Fourier Transform Infrared Spectroscopy

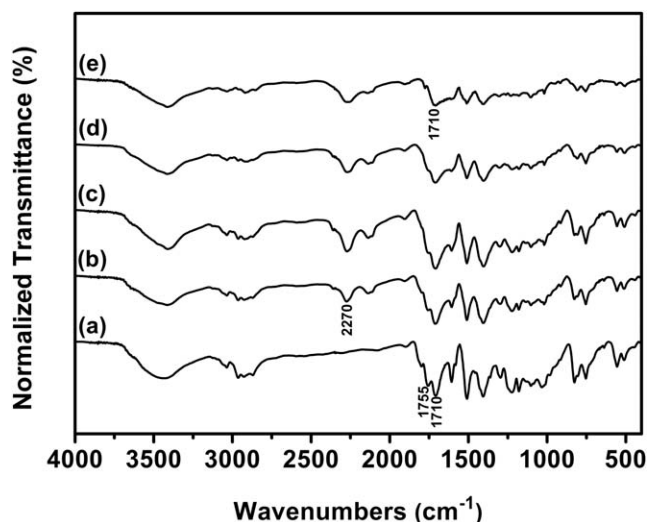
A Bruker TENSOR 27 (Bruker Corporation, Karlsruhe, Germany) Fourier transform infrared spectroscope (FTIR) was used to test the chemical structure of the foams cured at the different temperatures. All of the samples were mixed with potassium bromide (KBr) powder. The samples were scanned in transmission mode from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>.

### Dynamic Mechanical Analysis

The dynamical mechanical analysis (DMA) of EP-PIR foams was carried out with a TA Instruments DMA Q800 (TA Instruments, New Castle, Delaware). The dimensions of the samples were 45 mm × 12.7 mm × 2 mm. The frequency was fixed at 1 Hz. The samples were heated at 3°C/min from room temperature to 325°C.



**Scheme 2.** The generation of oxazolidone ring from isocyanurate.



**Figure 2.** FTIR spectra of EP-PIR foams with different mole ratios of [PAPI]/[DGEBA]: (a) 1, (b) 2.5, (c) 4, (d) 8, and (e) pure PIR foam. The cured temperature is 220°C for 2 h.

### Thermal Properties

Differential scanning calorimetry (DSC) was performed with a TA Instruments Q200 (TA Instruments, New Castle, Delaware) differential scanning calorimeter using a sample weight of around 5 mg with a heating rate of 10°C/min over the temperature range of 25 to 400°C under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out using a TA Instrument 2050 (TA Instruments, New Castle, Delaware). Temperature programs were run from room temperature to 700°C at a heating rate of 10°C/min under a nitrogen atmosphere.

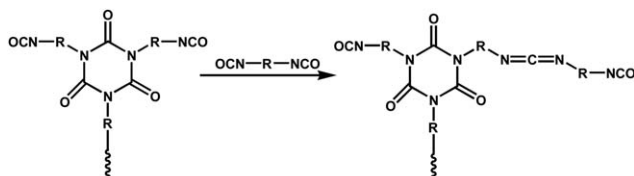
### Mechanical Properties

Compressive tests were performed with an Instron 5500 (Instron Corporation, Boston, Massachusetts) following the standard method. The dimensions of the samples were  $\Phi$  20 mm  $\times$  20 mm (diameter and height, respectively), and at least four specimens were measured to obtain average values. Samples were compressed between two stainless-steel platens using a cross-head rate of 2.0 mm/min. From the stress-strain curve, the compressive modulus was determined using the steepest initial slope.

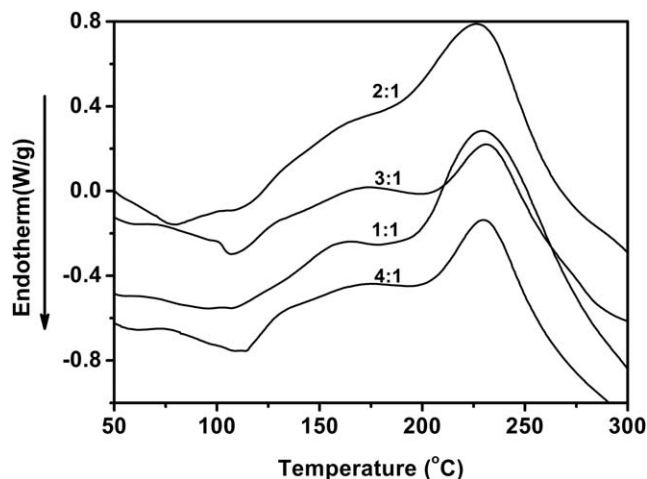
## RESULTS AND DISCUSSION

### Preparation of the EP-PIR Foams

The EP-PIR foams are prepared by reacting PAPI with DGEBA, and the mole ratio of [PAPI]/[DGEBA] is 2.5. According to previous reports, the curing temperature had a great influence on the chemical structure of the final EP-PIR resins.<sup>20</sup> Therefore,

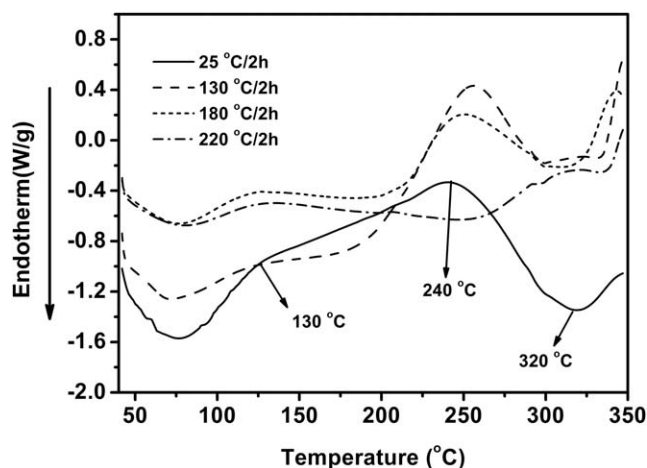


**Scheme 3.** The generation of carbodiimide group via the polycondensation of isocyanate.

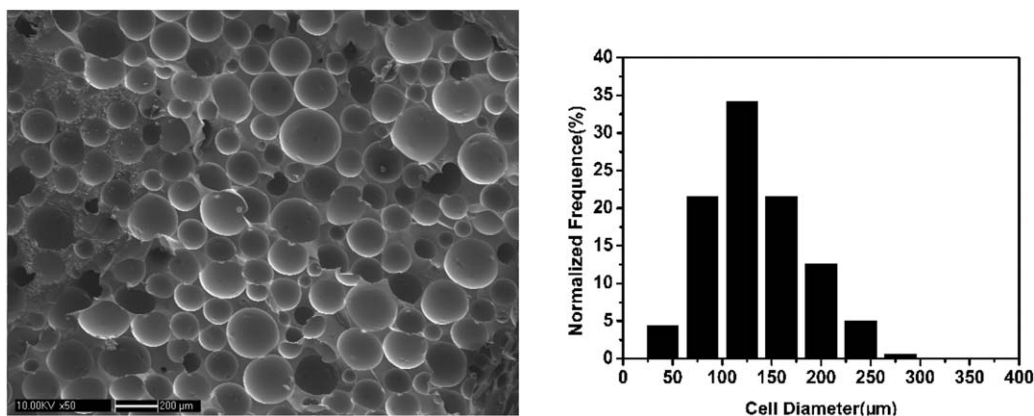


**Figure 3.** DSC thermograms of the EP-PIR foams cured at 25°C with different ratios of [PAPI]/[DGEBA].

the EP-PIR foams are postcured at 75°C, 100°C, 150°C, 180°C, and 220°C for 2 h. The FTIR spectra of EP-PIR foams cured at different temperatures are presented in Figure 1, and the mole ratio of [PAPI]/[DGEBA] is 2.5. In order to eliminate the effect of sample concentration on the peak intensity, the FTIR spectra are normalized by the peak value at 2964  $\text{cm}^{-1}$ , which is the stretching vibration peak of  $-\text{CH}_3$ . The strong absorption peak at 1710  $\text{cm}^{-1}$  is the characteristic absorption of the carbonyl group of isocyanurate rings. This indicates that the isocyanurate rings are generated at a low curing temperature due to the catalyst DMP-30. However, with the increase of the curing temperature, the intensity of the peak at 1710  $\text{cm}^{-1}$  decreases. This is because some of the isocyanurate rings transform into oxazolidone rings with the increase in temperature, as shown in Scheme 2.<sup>21</sup> A weak absorption at 1776  $\text{cm}^{-1}$  emerges at a low curing temperature of about 100°C, which belongs to a dimer of PAPI. With increasing curing temperature, the intensity of peaks at 2270  $\text{cm}^{-1}$  and 913  $\text{cm}^{-1}$  gradually decrease, which belong to  $-\text{NCO}$  and epoxy groups, respectively.<sup>22,23</sup> When the



**Figure 4.** DSC thermograms of the EP-PIR foams with different cure temperatures; the mole ratio of [PAPI]/[DGEBA] is 2.5: (a) 25°C for 2 h, (b) 130°C for 2 h, (c) 180°C for 2 h, (d) 220°C for 2 h.



**Figure 5.** SEM morphology and bubble size distribution of EP-PIR foams with the mole ratio of [PAPI]/[DGEBA] = 2.5. The density range is  $0.463 \pm 0.002 \text{ g/cm}^3$ .

curing temperature is  $220^\circ\text{C}$ , the peak of the epoxy group at  $913 \text{ cm}^{-1}$  disappears due to transformation to an oxazolidone ring. Similarly, when the curing temperature is above  $180^\circ\text{C}$ , a new absorption peak at  $1755 \text{ cm}^{-1}$  emerges, which is the carbonyl group peak of the oxazolidone ring.<sup>24</sup>

The FTIR spectra of EP-PIR foams prepared with different mole ratios of [PAPI]/[DGEBA] are shown in Figure 2. For pure PIR foam, the characteristic peak of the oxazolidone ring at  $1755 \text{ cm}^{-1}$  disappears (Figure 2e). When the mole ratio of [PAPI]/[DGEBA] is 1, the  $-\text{NCO}$  and epoxy groups are consumed completely, and the peaks at  $2270 \text{ cm}^{-1}$  and  $913 \text{ cm}^{-1}$  disappear, as shown in Figure 2a. When the mole ratio of [PAPI]/[DGEBA] is above 1, the absorption peak of  $-\text{NCO}$  at  $2270 \text{ cm}^{-1}$  still exists due to the excessive isocyanate. Furthermore, an absorption peak at  $2125 \text{ cm}^{-1}$  is observed, which is the typical absorption of the carbodiimide group (Scheme 3).<sup>25</sup>

The DSC thermograms of the EP-PIR foams cured at  $25^\circ\text{C}$  with different ratios of [PAPI]/[DGEBA] are shown in Figure 3. The exothermic peak at  $130^\circ\text{C}$  is the trimerization of isocyanate to form isocyanurate rings, and an exothermic peak at around  $170^\circ\text{C}$  is related to the formation of oxazolidone rings by reaction between isocyanate and epoxy groups. Meanwhile, the exothermic peak at  $220\text{--}240^\circ\text{C}$  is due to the formation of oxazolidone

rings by the reaction between isocyanate and epoxy groups (Scheme 2).<sup>20</sup> In Figure 3, the intensity of the exothermic peak at  $130^\circ\text{C}$  decreases with the decrease of the ratio of [PAPI]/[DGEBA]. When the ratio of [PAPI]/[DGEBA] is 1:1, the exothermic peak at  $130^\circ\text{C}$  even disappears. This result indicates that the increase of [DGEBA] can restrain the trimerization of isocyanate and promote the formation of oxazolidone rings.

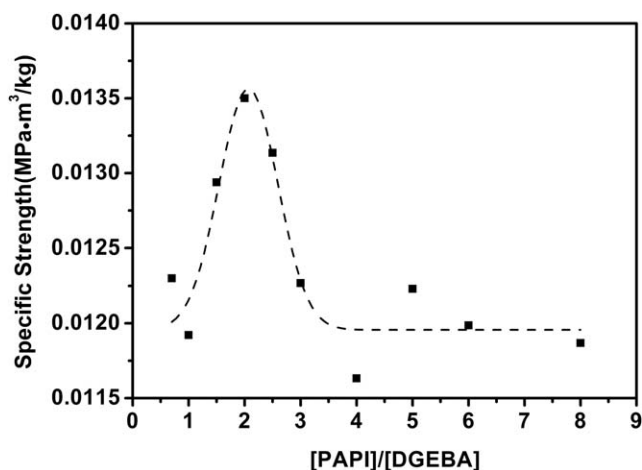
The influence of cured temperature on exothermic peaks has also been investigated, as shown in Figure 4. With the increase of cured temperature, the enthalpies of the exothermic peaks decrease gradually. When the foam is cured at  $220^\circ\text{C}$  for 2 h, the exothermic peak at  $240^\circ\text{C}$  disappears, which indicates the complete conversion of epoxy. Meanwhile, due to the excessive isocyanate, the exothermic peak at  $130^\circ\text{C}$  still exists. However, the intensity becomes much weaker, which is due to the steric hindrance effect. Those results agree well with the FTIR analysis.

#### Morphology and Mechanical Properties of EP-PIR Foams

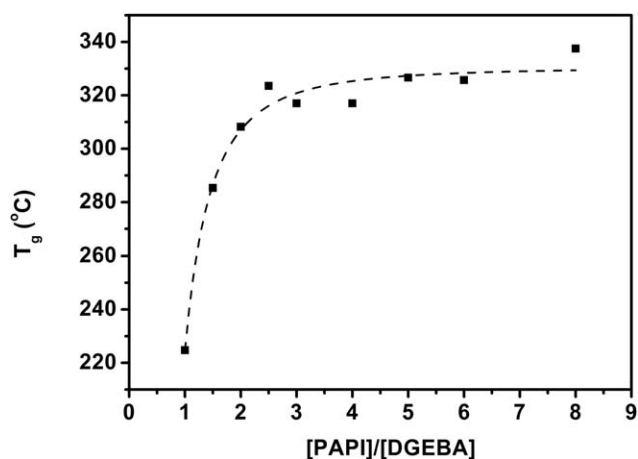
Figure 5 shows the SEM morphology and bubble size distribution of EP-PIR foams. The mole ratio of [PAPI]/[DGEBA] is 2.5. The SEM images (Figure 5) of the foam indicate that a closed-cell porous morphology is obtained, and the average cell size is  $135 \pm 48 \mu\text{m}$ .

**Table I.** Mechanical Properties of the EP-PIR Foams with Different Mole Ratios of [PAPI]/[DGEBA]

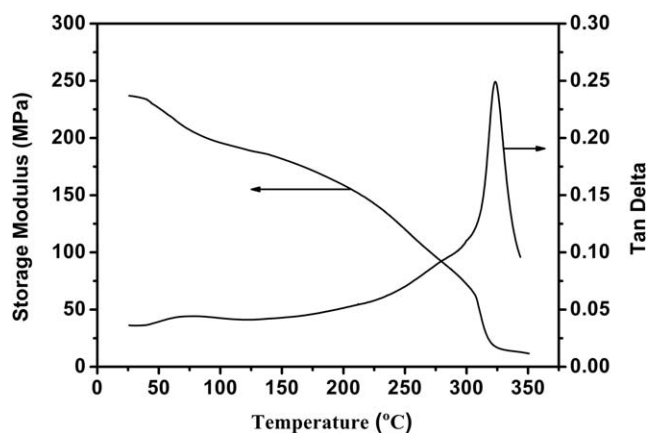
Sample	[PAPI]/[DGEBA]	Density ( $\text{kg/m}^3$ )	Strength (MPa)	Modulus (MPa)	Specific strength ( $\text{MPa m}^3/\text{kg}$ )
1	0.7	$379 \pm 2$	$4.66 \pm 0.10$	$477 \pm 11.1$	$0.0123 \pm 0.0003$
2	1.0	$406 \pm 2$	$4.84 \pm 0.07$	$494 \pm 12.3$	$0.0119 \pm 0.0002$
3	1.5	$422 \pm 2$	$5.46 \pm 0.06$	$560 \pm 14.3$	$0.0129 \pm 0.0002$
4	2.0	$420 \pm 1$	$5.67 \pm 0.13$	$604 \pm 26.6$	$0.0135 \pm 0.0003$
5	2.5	$405 \pm 1$	$5.32 \pm 0.09$	$549 \pm 11.5$	$0.0131 \pm 0.0003$
6	3.0	$388 \pm 4$	$4.76 \pm 0.17$	$482 \pm 16.0$	$0.0123 \pm 0.0006$
7	4.0	$386 \pm 3$	$4.49 \pm 0.18$	$466 \pm 17.4$	$0.0116 \pm 0.0006$
8	5.0	$417 \pm 4$	$5.10 \pm 0.26$	$535 \pm 25.8$	$0.0122 \pm 0.0007$
9	6.0	$423 \pm 3$	$5.07 \pm 0.51$	$538 \pm 16.5$	$0.0120 \pm 0.0013$
10	8.0	$380 \pm 12$	$4.51 \pm 0.16$	$475 \pm 22.3$	$0.0119 \pm 0.0008$



**Figure 6.** Effect of [PAPI]/[DGEBA] on the specific compressive strength of EP-PIR foam.



**Figure 9.** Effect of [PAPI]/[DGEBA] on the glass-transition temperature of EP-PIR foam.



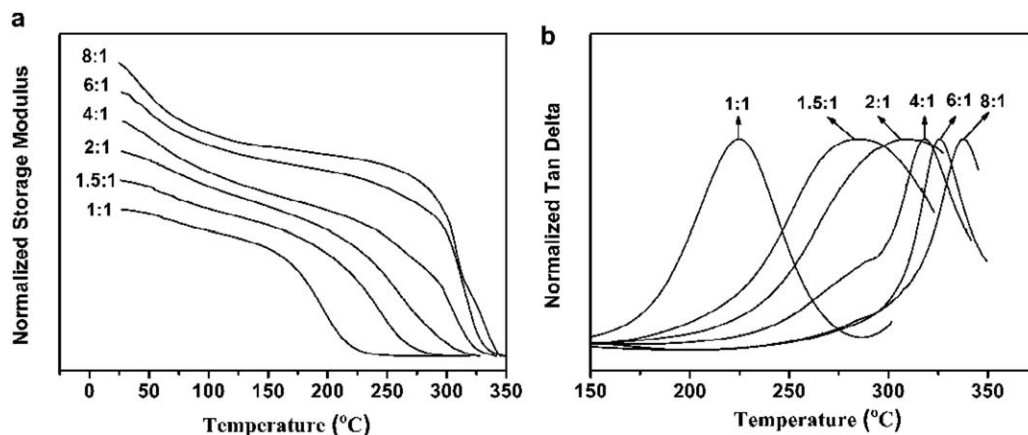
**Figure 7.** Temperature dependence of storage modulus and  $\tan \delta$  for the EP-PIR foams. The mole ratio of [PAPI]/[DGEBA] is 2.5.

Table I shows the mechanical properties in compression for the EP-PIR foams with different mole ratios of [PAPI]/[DGEBA]. To investigate the influence of mole ratio of [PAPI]/[DGEBA] on the mechanical properties, the specific properties (property/density) of foams are calculated. Figure 6 shows the influence of

[PAPI]/[DGEBA] on the specific compressive strength of EP-PIR foams. When the mole ratio of [PAPI]/[DGEBA] is 2, the specific compressive strength shows a maximum of  $0.0135 \pm 0.0003$  MPa m<sup>3</sup>/kg. However, with the increase of [PAPI]/[DGEBA], the specific compressive strength decreases dramatically and then stays constant. This may be explained by the transformation of molecular structures. Generally, the EP-PIR foams contain two main molecular structures, which are the linear oxazolidone ring and the crosslinked isocyanurate ring. When the mole ratio of [PAPI]/[DGEBA] is below 2, the reaction of —NCO and epoxy to form a linear oxazolidone ring is dominant. Therefore, with the increase of [PAPI]/[DGEBA], the concentration of crosslinked isocyanurate rings increases and results in the increase of mechanical properties. However, excessive [PAPI]/[DGEBA] makes the crosslinked isocyanurate ring dominant, which would improve the brittle property and result in a decrease in specific compressive strength.

#### Thermal Stability of EP-PIR Foam

The thermal properties of thermosets are known to be dependent on their molecular structures. DMA is generally recognized to be sensitive to molecular motions and useful for evaluating subtle transitions occurring in a polymeric system.<sup>26,27</sup> The



**Figure 8.** Temperature dependence of (a) storage modulus and (b)  $\tan \delta$  for EP-PIR foams with various [PAPI]/[DGEBA] ratios.

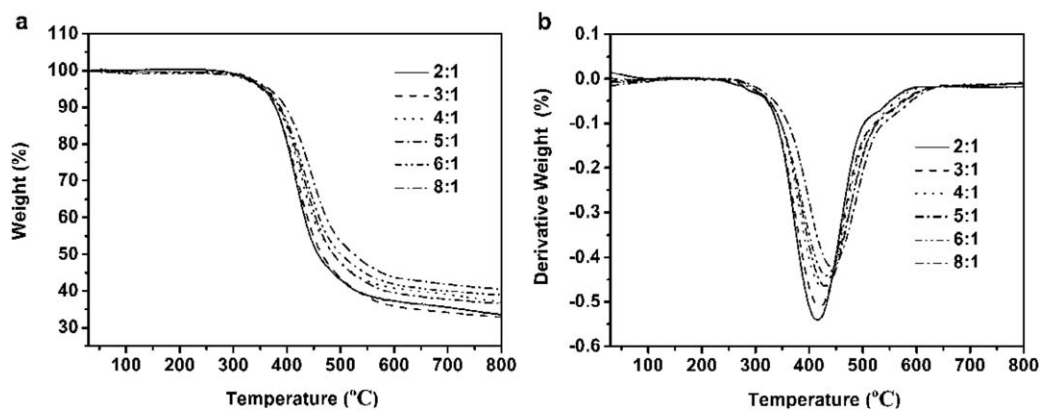


Figure 10. (a) TGA and (b) DTG curves of the EP-PIR foams with different ratios of [PAPI]/[DGEBA].

viscoelastic parameters, the onset point of storage modulus and the  $\tan \delta$  peak, can both reflect the glass transition of the polymer.<sup>28</sup> Figure 7 shows the dynamic mechanical properties of EP-PIR foam, and the mole ratio of [PAPI]/[DGEBA] is 2.5. The results show that the storage modulus decreases gradually with increasing temperature until a sharp decrease, which is attributed to the glass-transition temperature ( $T_g$ ) at 323.5°C. However, there are two peaks of secondary relaxation and transition at 75°C and 275°C, respectively. The peak at 75°C belongs to the secondary relaxation of the DGEBA polyether, which is formed via the homopolymerization of DGEBA.<sup>20</sup> The peak at 275°C belongs to the secondary transition of a linear oxazolidone.

The influences of mole ratio of [PAPI]/[DGEBA] on the storage modulus and  $\tan \delta$  are also shown in Figure 8. With the increase of [PAPI]/[DGEBA], the glass-transition temperature trends to move to higher temperature, due to the formation of highly crosslinked six-member isocyanurate rings. A plot of the [PAPI]/[DGEBA] against the  $T_g$  is shown in Figure 9. The results indicate that the  $T_g$  of the sample increases quickly. However, when the mole ratio of [PAPI]/[DGEBA] reaches 2.5, the  $T_g$  meets a transition point and then trends to be constant. These results indicate that the optimum mole ratio of

[PAPI]/[DGEBA] is around 2.5 to reach the better mechanical and thermal properties.

Figure 10 shows the TGA and DTG curves of the foams with different mole ratios of [PAPI]/[DGEBA]. The onset of weight loss taken at 5% is defined as the initial decomposition temperature ( $T_{\text{initial}}$ ), and a plot of [PAPI]/[DGEBA] against  $T_{\text{initial}}$  and peak decomposition temperature ( $T_p$ ) is presented in Figure 11. The results indicate that the  $T_{\text{initial}}$  and  $T_p$  increase proportionally with the increasing ratio of [PAPI]/[DGEBA]. Meanwhile, the solid residue yields of all foams, which are attributed to the formation of residual carbon,<sup>29</sup> are above 33 wt % and increase with the ratio of [PAPI]/[DGEBA]. These results indicate that the EP-PIR foams possess outstanding thermostability.

## CONCLUSIONS

A series of EP-PIR foams with OX and IS rings were prepared by the reaction of PAPI and DGEBA, and DMP-30 was used as a catalyst. The influences of the initial composition of the formulation and the curing conditions on the final chemical structure are investigated. FTIR and DSC results indicate that low temperature is beneficial to the formation of IS rings, and high temperature is beneficial to the OX rings. SEM images show that the average cell size is  $135 \pm 48 \mu\text{m}$  for the EP-PIR foam with a density of  $0.463 \pm 0.002 \text{ g/cm}^3$ .

The influence of the mole ratio of [PAPI]/[DGEBA] on the mechanical properties and thermal stability has also been studied. With the increase of [PAPI]/[DGEBA], the specific compressive strength shows a maximum of  $0.0135 \pm 0.0003 \text{ MPa m}^3/\text{kg}$ . However, excessive [PAPI]/[DGEBA] will increase the crosslinked density and the brittleness, which will decrease the mechanical properties. The optimum mole ratio of [PAPI]/[DGEBA] is around 2.5 to reach the better mechanical and thermal properties, and the glass-transition temperature is as high as 323.5°C. The TGA results show that the  $T_{\text{initial}}$  and  $T_p$  increase proportionally with an increasing ratio of [PAPI]/[DGEBA], and the solid residue yields after reaching 800°C are all above 33 wt %. These results indicate that the EP-PIR foams have excellent thermal stability and mechanical properties, which opens up a range of potential applications in naval vessels, military vehicles, and aircraft.

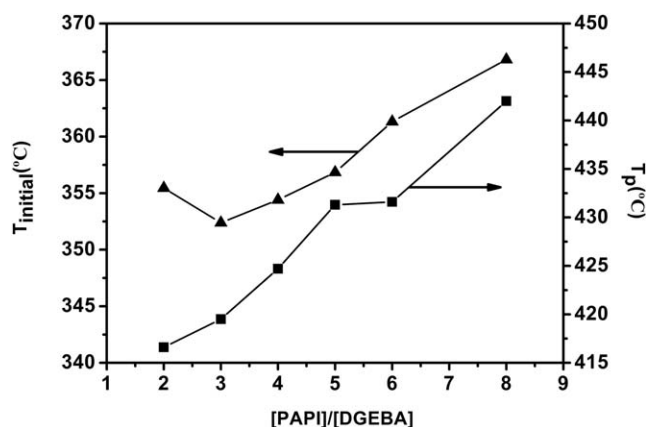


Figure 11. Effect of [PAPI]/[DGEBA] on the initial decomposition temperature ( $T_{\text{initial}}$ ) and peak decomposition temperature ( $T_p$ ) of the EP-PIR foams.

## ACKNOWLEDGMENTS

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