Poly(ether imide)/Epoxy Foam Composites with a Microcellular Structure and Ultralow Density: Bead Foam Fabrication, Compression Molding, Mechanical Properties, Thermal Stability, and Flame-Retardant Properties

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ABSTRACT: It is challenging to prepare ultralow-density microcellular foams based on high-performance polymers due to their low gas solubility and rigid polymer matrix. In this study, by applying microcellular foaming technology using CO2/acetone as the blowing agent, ultralow-density poly(ether imide) (PEI) bead foams with an expansion ratio of 30–56 times and cell density of $10^7–10^9$ cells/cm$^3$ were fabricated, resulting from the enhanced plasticization effect of the mixed fluid. The slow diffusivity of acetone at room temperature ensured the saturated PEI beads to foam after desorption for more than 6 days, which potentially reduces the transportation cost of PEI bead foams significantly. A novel compression molding process was developed to prepare the molded PEI bead foams (MPEIs) using epoxy as a coating agent. The good infiltration character of epoxy on bead foams endowed the MPEIs with excellent mechanical properties, together with an ultralow density of 80–200 kg/m$^3$, long-term dimensional stability at 160 °C, and excellent flame-retardant properties of V0 rating. These features made the MPEIs very promising for many advanced applications.

1. INTRODUCTION

Polymeric foams have been widely used in many applications such as packaging, cushioning, construction, and electronic apparatus due to their high strength-to-weight ratio, excellent heat and sound insulation, high energy absorption, lightweight nature, and so on.1–3 Bead foam is one type of the most important polymeric foams. Different from the extruded foam and injection molded foam, bead foam has the advantages of extremely high foam expansion ratio up to 40–60 times, flexible product size control, comparatively low manufacturing cost, and the ability to fabricate into complex three-dimensional shape.4 Moreover, there are so many available and potential candidates for bead foam to satisfy various applications. Expandable polystyrene (EPS) is the most commonly used bead foam, and it has been used in packaging and thermal insulation materials for many years due to its low cost. However, its poor mechanical properties, low service temperature, and environmental concern limit its usage. To address these problems, expanded polyethylene (EPE) and expanded polypropylene (EPP) were developed in the 1970s to 1980s. EPP has excellent mechanical properties, which is why it is used in the automotive field as a core material for bumper impact protection.5 In addition, EPP products are beginning to be used now in more complex applications such as energy management, acoustic preference, and structure support.1 To relieve the environmental pressure of discarded foams, expanded polylactide (EPLA) has been developed in recent years.7–9 According to the experimental results, EPLA exhibited comparable mechanical properties with that of EPS,7 but it could be biodegraded in landfill within a couple of months. Besides the rigid foams, a novel flexible bead foam, that is, expanded thermoplastic polyurethane (ETPU), has been produced for use in cushioning and sport protection.10,11 Engineer polymers such as PBT had also been fabricated into bead foams (EPBT),12 with the aim of further improving the mechanical properties and thermal stability of bead foams, and those foams have been potentially used in the foam core of composites. Recently, researchers have pursued to prepare some advanced polymeric bead foams based on high-performance polymers,13 and the prepared foams could handle
higher requirements of service temperature, flame rating, and so on.
Poly(ether imide) (PEI), polyimide (PI), poly(ether sulfone) (PES), and polysulfone (PSU) are high-performance polymers with excellent intrinsic flame-retardant performance. Microcellular or nanocellular foams based on those materials have been developed by using compressed CO₂ as a blowing agent or using a water-vapor-induced phase separation process, where cells with sizes in the range of 1–100 μm or 100–500 nm are generated. The generated fine cell structure endows the as-prepared high-performance foams with uncompromised mechanical properties, excellent flame retardancy, improved toughness, and low-k value. However, for these high-performance resins, using pure CO₂ as a blowing agent to prepare foams with expansion ratio higher than 10 times is a challenge, regardless of whether temperature rising or pressure quenching foaming processes are conducted. Another challenge of microcellular foaming of high-performance polymers is long saturation time, such as 280 h at 5 MPa for the saturation of PEI sheet with a thickness of 1.5 mm using CO₂ as a blowing agent, which inevitably restricts the commercial application of microcellular foaming technology in fabrication of large-sized microcellular foam.

To solve these problems, an organic solvent (tetrahydrofuran) had been used as a coblowing agent of compressed CO₂ to prepare microcellular PI foam in our previous work, where PI beads with a diameter of 1.2–1.4 mm and aspect ratio of 1.5–2.0 were used. It had been verified that the mixed fluid exhibited increased solubility from 4.2% (pure CO₂) to 24.0%, and microcellular PI foams with an expansion ratio of 15–18 times were fabricated. Meanwhile, using bead-shaped PI resin, a short saturation time of about 24–48 h was enough to achieve the dissolution equilibrium of the mixed fluid, and about 10 kg of bead foams could be prepared each time by a laboratory-scale device. In a recent study, ethanol was selected as a coblowing agent of compressed CO₂ to foam PI bead, and an increased expansion ratio of PEI microcellular foam (from 3.5 times to 7.2 times) was achieved. Based on our knowledge, however, there is no report about the preparation of ultralow-density bead foams based on high-performance polymers, where the expansion ratio of bead foams is as high as 30 times.

In this study, the main targets are to fabricate the ultralow-density PEI bead foams with a microcellular structure and expansion ratio higher than 30 times and then mold them into a large-sized sample. Acetone has strong polarity, presents a high solubility in PEI resin, and cannot dissolve PEI resin. The mixed CO₂/acetone fluid was used as a blowing agent to foam PEI beads by the solid-state foaming process. The dissolution and desorption behavior were investigated to present the influence of acetone addition on the diffusion kinetics of mixed fluid. Ultralow-density PEI bead foams with an expansion ratio of 30–56 times could be prepared at a quite broad foaming window. Saturation pressure, foaming temperature, and desorption time were verified as critical parameters to control the cell morphology and expansion ratio of expanded PEI (EPEI) beads. The mechanism of PEI foaming was discussed based on the competing cell growth, gas escape, and mass transport resistance of the plasticized polymer phase. A novel compression molding process was carried out to prepare the MPEIs using epoxy as a coating agent. The infiltration character of epoxy on EPEI beads was analyzed, and the epoxy concentration and compression degree were changed to adjust the inter bead bonding behavior. In the last part of this study, the mechanical properties, long-term thermal stability, and flame-retardant properties of MPEIs were investigated to illustrate their good performance.

2. RESULTS AND DISCUSSION

2.1. Solubility and Desorption Behavior of CO₂/Acetone in PEI. The low gas solubility and poor plasticization effect of physical blowing agent have been verified as the main challenge to fabricating low-density-high-performance polymeric foams. To increase the solubility of blowing agent in PEI, an organic solvent, acetone, was used as a coblowing agent together with compressed CO₂ in this study. Table 1 summarizes the CO₂/acetone solubility in PEI as a function of CO₂ pressure. As expected, the compressed CO₂ exhibits poor solubility in the PEI matrix, that is, 3.1% at 1 MPa, 4.8% at 3 MPa, and 5.6% at 5 MPa. These CO₂ solubility data are much less than those of other polymers, such as 19.2% at 5 MPa/25 °C for PLA, 8.7% at 5 MPa/35 °C for PS, and 12.5% at 5 MPa/35 °C for PMMA. Based on the free volume theory, a polymer that possesses a higher T₆ has less free volume to be occupied by CO₂ molecules among polymer chains than the one with a lower T₆, which could be the reason why the compressed CO₂ exhibited low solubility in PEI. The solubility of liquid acetone in PEI was 27.0% at 25 °C and atmospheric pressure, and this value reduced to 12.7% at 60 °C, where acetone was in gas state. No matter what state acetone was in, it exhibited much higher solubility in PEI than compressed CO₂, which might be attributed to the stronger polarity of acetone.

The influence of acetone addition on the CO₂/acetone solubility in PEI was investigated, and the results are also presented in Table 1. At a CO₂ pressure of 1 MPa, the solubility of mixed CO₂/acetone fluid in PEI was 24.2%, which was about seven times higher than the solubility of pure CO₂. It suggests that the presence of acetone significantly improved the solubility of mixed fluid in PEI. With the increase in CO₂ pressure, however, the solubility of mixed fluid gradually reduced to 23.2% at 2 MPa, to 15.4% at 4 MPa, and to 14.5% at 6 MPa. It is surprising to see these results since the increased CO₂ pressure usually increased the solubility of CO₂ in polymers. Considering that acetone exhibited lower solubility at 60 °C compared to that at room temperature, 12.7% vs 27.0%, we believed that acetone in the PEI matrix could be partially replaced by CO₂ during the saturation process, and

Table 1. CO₂ and Acetone/CO₂ Solubility of PEI Saturated at 60 °C and Various CO₂ Pressures

| item | CO₂ pressure* (MPa) | CO₂ solubility (%) | acetone/CO₂ solubility (%) |
|------|---------------------|--------------------|---------------------------|
|      | 0                   | 1                  | 2                          | 3              | 4               | 5               | 6               |
|      |                     | 3.1                | 4.8                        | 5.6            |
|      | 27.0*               | 24.2               | 23.2                       | 18.0           | 15.4            | 14.9            | 14.5            |
|      | 12.7*               |                    |                            |                |                |                |

*The specimens were saturated by compressed CO₂ at 60 °C and various pressures. PEI beads were soaked in liquid acetone at room temperature and atmospheric pressure for 2 weeks. PEI beads were saturated by gaseous acetone at 60 °C and saturation vapor pressure for 2 weeks (the boiling point of acetone is 56 °C)
the enhanced CO₂ replacement would reduce the whole solubility of mixed fluid.

Rapid gas escape is a typical character of CO₂ blowing agent during foaming;³⁴,³⁵ therefore, unlike the preparation of EPS beads with using n-pentane (with a low diffusivity) as a blowing agent, the gas-saturated PP, PLA, and TPU beads must be expanded right away.⁴,⁷,³⁶ As a consequence, EPP, EPLA, and ETPU beads have large volume, which leads to costly transportation.⁵ The influence of acetone addition on CO₂ escape as a function of desorption time is shown in Figure 1. It is seen that the uptake of mixed fluid reduces rapidly within 10 h and then levels off at a desorption time longer than 40 h. The residual fluid solubility is about 8%, and this value is quite stable at a desorption time of 50~140 h. These interesting results seemed to suggest that the mixed fluid could be stored within PEI for more than 5 days at room temperature and atmospheric pressure. This long-time storage of blowing agent in polymer beads is meaningful for bead foam transportation. During the EPLA bead process, researchers had carried out a low-temperature storage of CO₂-impregnated PLA beads at −18 °C.³⁷ The absorbed CO₂ could stay in PLA longer since low temperature could reduce gas diffusivity. However, it seems that this method was not cost-effective due to the additional refrigeration cost.

2.2. Foaming Behavior of PEI Beads Blown with CO₂/Acetone. A solid-state foaming method was conducted to foam PEI beads, where the acetone-soaked PEI beads were saturated by compressed CO₂ at 60 °C and various pressures, and then the as-obtained PEI beads were foamed by hot air at different temperatures for 1 min. Figure 2 shows a comparative result of EPEI beads blown with pure CO₂, pure acetone, and mixed CO₂/acetone fluid. As shown in Figure 2A, PEI beads are transparent yellow column with a diameter of about 1.0 mm and length of about 1.2 mm. After being foamed by the mixed fluid, PEI beads became white with light yellow, and the volume expanded significantly as indicated in Figure 2B. Specifically, the diameter of EPEI beads increased up to 5.0 mm, which suggested a 40~50 times expansion in volume after foaming.

The cell morphology change of EPEI beads with the blowing agents is also indicated in Figure 2. In the case of pure CO₂, the prepared EPEI beads had a 2.8 times expansion ratio, fine cell size of about 13.5 μm, and high cell density of about 7.5 × 10⁹ cells/cm³. When acetone was used as a blowing agent, PEI beads could be highly expanded, and the obtained EPEI beads

Figure 1. Uptake of mixed fluid in PEI beads as a function of desorption time. The inset is the uptake data of mixed fluid at a short desorption time. The PEI beads were soaked in acetone at room temperature and atmospheric pressure for 2 weeks, and the soaked PEI beads were saturated by compressed CO₂ at 60 °C and various pressures for 48 h.

Figure 2. (A) Optical micrographs of PEI beads. (B) EPEI beads blown with acetone/CO₂ and (C–E) cell morphologies of EPEI beads blown with acetone/CO₂ (C), pure acetone (D), and pure CO₂ (E).
had a 3.56 times expansion, but with a large cell size of about 425.0 μm and low cell density of about 1.5 × 10^8 cells/cm^3. When the mixed CO2/acetone fluid was selected as a blowing agent, EPEI beads with an expansion ratio of 46.7 times were fabricated; meanwhile, EPEI beads exhibited a fine cell size of about 95.0 μm and cell density of about 1.1 × 10^9 cells/cm^3. These results suggested that the as-obtained EPEI beads blown with mixed fluid possessed an ultralow density of 0.028 g/cm^3, as well as the microcellular structure.

2.2.1. Effect of Foaming Temperature. Foaming temperature is a critical foaming parameter to illustrate the foaming window of polymer. The influence of foaming temperature on the expansion ratio of EPEI beads is presented in Figure 3.

![Figure 3](https://dx.doi.org/10.1021/acsomega.0c03072)

**Figure 3.** Expansion ratio of EPEI beads obtained at various saturation pressures and foaming temperatures, blown with acetone/CO2. The PEI bead foam with expansion ratio higher than 30 times was defined as the ultralow-density foam, and a foaming window to generate these foams was obtained as pointed by the black arrow.

where the saturation pressures were 1−5 MPa, and acetone/CO2 fluid was used as the blowing agent. The mountain-shaped curves of expansion ratio as a function of foaming temperatures were observed, and the optimum foaming temperature was 240 °C, which corresponded to the largest expansion ratio of 54.4 times at 1 MPa. This typical mountain shape had been widely reported in polymer autoclave foaming systems, such as PLA foaming. The upward trend of curves’ left side resulted from the reduced matrix modulus with increasing foaming temperature, which facilitated cell growth and foam expansion. On the other hand, the downward trend of curves’ right side was caused by the accelerated gas escape due to the decreased melt strength at higher foaming temperatures. The foam with expansion ratio higher than 30 times is usually defined as ultralow-density foam. In this study, a broad foaming temperature window of about 25 °C could be used to fabricate ultralow-density PEI foam at 1 MPa, and an increase in saturation pressure tended to narrow the foaming temperature window to 20 °C at 3 MPa and to 10 °C at 5 MPa due to the reduced solubility of mixed fluid.

Figure 4 shows the cell morphology evolution of EPEI beads as a function of foaming temperature, and Figure 5 summarizes the average cell size and cell density data of the foams. All EPEI beads possess polygonal cell morphology and a well-defined closed cell structure. An increase in foaming temperature tended to increase the average cell size gradually from 32.5 μm at 180 °C up to 120.1 μm at 240 °C, which was associated with the volume expansion of EPEI beads. At a higher foaming temperature of 250 °C, however, the average cell size reduced rapidly to 102.5 μm. The cell density of EPEI beads does not change obviously at the applied foaming temperatures, as shown in Figure 5, which suggested that no observable cell coalescence occurred during foaming.

2.2.2. Effect of Saturation Pressure. The influence of saturation pressure on the foaming behavior of PEI beads was investigated, where the acetone-soaked PEI beads were saturated by CO2 with pressures of 1−6 MPa and then foamed at 240 °C for 1 min. Figure 6 shows the cell morphology and the corresponding average cell size and cell density of EPEI beads are summarized in Figure 7. The as-prepared EPEI beads blown with mixed fluid had fine cells and uniform cell structure distribution. Compared with EPEI beads prepared by pure acetone, the introduction of CO2 significantly decreased the cell size from 275.4 to 123.2 μm and the cell density is substantially increased by about two orders of magnitude, that is, from 5.2 × 10^4 to 3.2 × 10^6 cells/cm^3. With further increase in CO2 pressure, the cell size of EPEI beads decreased gradually to 37.5 μm and the cell density increased up to 3.5 × 10^8 cells/cm^3 at 6 MPa, indicating the formation of microcellular foam.

2.2.3. Effect of Desorption Time. Desorption time is another critical parameter for solid-state foaming of polymers. In general, researchers try to shorten the desorption time as short as possible because the saturated CO2 fluid can escape out of the polymer matrix after depressurization, which tends to increase the thickness of unfoamed skin layer and decrease the volume expansion of the prepared foams. The CO2/acetone-saturated PEI beads at 3 MPa and 60 °C were desorbed from 5 h to 6 days under 25 °C and atmospheric pressure and then were foamed at 240 °C for 1 min. The scanning electron microscopy (SEM) images presented in Figure 8 illustrate the cell morphology of EPEI beads as a function of desorption time, and the corresponding foam expansion, average cell size, and cell density of bead foams are summarized in Figure 9. It can be seen from Figure 8 that all EPEI beads prepared at the selected desorption times had polygon cell morphology and uniform cell structure distribution. Figure 9 shows that EPEI beads have a high expansion ratio of 41.5 times, cell size of 87.5 μm, and cell density of 9.8 × 10^7 cells/cm^3 at a desorption time of 5 h. With the extension of desorption time to 1 day, the foam expansion of EPEI beads reduces to 39.7 times, the cell size increases to 92.5 μm, and the cell density decreases to 8.7 × 10^6 cells/cm^3. With further extension of the description time, the expansion ratio of EPEI beads decreases gradually to 27.2 times in 6 days. Meanwhile, under this condition, the cell size of EPEI bead increases up to 117.5 μm and the cell density decreases to 9.8 × 10^5 cells/cm^3. These results demonstrated that the mixed CO2/acetone fluid could diffuse out of the polymer matrix, which decreased the fluid uptake. Moreover, the cell nucleation and cell growth were weakened, resulting in the decreased cell density and foam expansion. Even though a large amount of fluid escaped, the amount of residual blowing agent after 5 days of desorption was still high enough to trigger cell nucleation and provide full cell growth, resulting in superlight PEI bead foams.

2.3. Mechanism of PEI Foaming Using CO2/Acetone Fluid as the Blowing Agent. Figure 10 shows the comparative expansion ratio data of the reported microcellular foams based on high-performance polymers, where micro-
cellular or nanocellular foams are prepared using a physical blowing agent. As indicated in Figure 10, when pure CO₂ was used as a blowing agent, no matter which foaming method is chosen, temperature rising process or pressure quenching process, the expansion ratio less than 10-fold was normally obtained. Using organic solvents such as tetrahydrofuran and ethanol as the coblowing agents, however, the dramatically increased foam expansion ratios could be achieved in PI and PEI bead foams, where maximum expansion ratios of 15–18 times and 7 times were obtained, respectively. In this study, with using acetone as a coblowing agent, EPEI beads with an ultralow density of 0.023 g/cm³ and ultrahigh expansion ratio of 56 times were prepared. Based on our knowledge, this is the first report about the fabrication of ultralow-density high-performance polymer microcellular foam using the physical foaming method.

It has been reported that the CO₂ solubility in high-performance polymers is about 3–6%. The introduction of an organic solvent in compressed CO₂ was verified to increase fluid solubility up to 14.2–18.9%, which facilitated foam expansion and the preparation of low-density PI (T_g of 265 °C) foam with an expansion ratio of about 15–18 times. However, the adjustment of saturation temperature, saturation pressure, foaming temperature, and foaming could not further increase the expansion ratio of PI bead foam anymore. In this study, PEI with T_g of 220 °C was selected, and both CO₂ and CO₂/acetone were used as the blowing agents. The results showed that the expansion ratios of the fabricated PEI bead foams were about 1.8–3.9 and 9.8–55.6 times, respectively. It was interesting to find that the solubility of both CO₂ and mixed fluid in both PI and PEI were similar; they were 3.0–5.1% vs 3.1–5.6% and 14.2–18.9% vs 14.5–24.2%, respectively. The critical questions are as follows: why PEI bead foam had a much higher expansion ratio than PI bead foam, and why PEI bead could foam after such a long desorption time? In the

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c03072)

**Figure 4.** SEM micrographs of EPEI beads obtained at various foaming temperatures. The PEI beads were saturated at 3 MPa and 60 °C for 24 h and then foamed at various temperatures for 1 min.

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c03072)

**Figure 5.** Average cell size and cell density of EPEI beads obtained at various foaming temperatures after being saturated by acetone/CO₂ at 3 MPa and 60 °C for 24 h, the saturated PEI beads were foamed for 1 min.
following, we try to explain the foaming mechanism of PEI bead blowing with CO2/acetone.

During the microcellular foaming process, the compressed fluid disperses within the polymer matrix homogeneously. The cell nucleation is triggered by pressure quenching or temperature rising and the dissolved gas diffusing into the nucleated bubbles induces cell growth. As illustrated in Figure 11, two competing processes can affect the cell growth process: one is the gas diffusion, which drives the cell growth, and the other is the mass transport resistance of the plasticized polymer phase to the deformation of bubbles.40 The growing bubble is somehow like a “leaky balloon”, the compressed gas within the bubble not only promotes bubble growth but also escapes out of the bubble, and an increase in temperature will enhance both of them. As shown in curves’ left side in Figure 3, an increase in foaming temperature could decrease the mass transport resistance of plasticized polymer phase and increase gas diffusivity, which facilitated cell growth and foam expansion. At higher foaming temperature such as 250 °C, the process of penetrant loss prevailed, and the diffusion of fluid to the outside of polymeric material determined the process.

An increase in fluid solubility in the polymer means increased polymer chain mobility, which tends to reduce the mass resistance of the plasticized polymer phase, and thus enhances cell growth. As mentioned above, the mixed fluids had similar solubility in both PI and PEI; however, the latter exhibited a much higher foam expansion during the solid-state foaming. The difference in Tg and matrix modulus could be the main reason for this phenomenon. It was believed that the higher mass resistance made more gas escape out of the bubble without being used for bubble growth during the PI foaming process, while the plasticized PEI possessed a lower mass resistance so that the dissolved gas preferred to expand the foam.

Besides the preparation of ultralow-density PEI foam, the other contribution of coblowing agent was the expandable character of the saturated PEI beads after 6 days of desorption. As indicated in Figure 1, about 9.2−7.8% residual of mixed fluid within PEI beads was observed after desorption of about 1−6 days, and this amount of blowing agent was enough to ensure a 40−28 times expansion of EPEI beads, as shown in Figure 9. It is known that the boiling point of acetone is 56 °C. Therefore, the dissolved acetone in the saturated PEI beads at room temperature was in liquid state. Acetone is one kind of polar solvent; it exhibits intermolecular interactions with the carbonyl group and benzene ring of the PEI molecular chain, resulting in low diffusivity. It is believed that the low diffusion rate of liquid acetone was a key reason why PEI beads possessed such high residual acetone even after desorption for 6 days. Moreover, Figures 8 and 9 show that the as-obtained EPEI beads exhibit a high cell density of about 107 cells/cm3 and small cell size of about 100−120 μm. Considering that acetone possessed much poor cell nucleation ability than compressed CO2 as indicated in Figure 2, we believed that there was a large amount of residual CO2 fluid in the PEI matrix after a long-time gas desorption, which could be attributed to the presence of synergistic effect between organic solvent and compressed CO2.28,42,43

Figure 6. SEM micrographs of EPEI beads obtained at various saturation pressures. The PI beads were saturated at 1−6 MPa and 60 °C for 24 h and then foamed at 240 °C for 1 min.

Figure 7. Average cell size and cell density of EPEI beads obtained at various saturation pressures, saturated by acetone/CO2 at 60 °C for 24 h. The saturated PEI beads were foamed at 240 °C for 1 min.
2.4. Compression Molding of EPEI Beads. Polymeric bead foams usually have to be molded before use, and steam chest molding is a commercial way to manufacture bead foam products. During the steam chest molding process, steam is used as heating medium to soften the beads’ surface and

Figure 8. SEM micrographs of EPEI beads obtained at various desorption times. The PEI beads were saturated by acetone/CO₂ at 3 MPa and 60 °C for 24 h and then foamed at 240 °C for 1 min.

Figure 9. (A) Expansion ratio. (B) Average cell size and cell density of EPEI beads obtained at various desorption times. The PEI beads were saturated by acetone/CO₂ at 3 MPa and 60 °C for 24 h and then foamed at 240 °C for 1 min.

Figure 10. Reported expansion ratio of high-performance polymer foams blown with compressed CO₂ and mixed fluids.

Figure 11. Schematic illustration of the saturation and foaming process (cell growth process) of PEI beads blown with CO₂/acetone mixed fluid.
induce the formation of interbead bonding via polymer chain diffusion and solidification at the beads’ interface. Due to temperature limitation of the commercially available steam chest molding, a novel compression molding process was conducted to fabricate the MPEIs in this study.

Figure 12 shows the compression molding process. Before the molding, EPEI beads were coated by epoxy resin with excellent flame-retardant properties. The reason why we selected the flame-retardant grade epoxy was that we did not want to spoil the potential flame-retardant performance of EPEI beads. The epoxy was blended with the diluting agent (acetone) with the aim of controlling the viscosity of epoxy. The epoxy-coated EPEI beads were put into the mold cavity, thermally compressed at 160 °C for 2 h. Subsequently, the epoxy layers solidified and generated strong interbead bonding among bead foams. As shown in Figure 12, the MPEIs with light weight and large size could be produced by this method.

The infiltration character of epoxy on EPEI beads determined the interface bonding behavior between EPEI beads and the epoxy interface layer, which would significantly affect the mechanical properties of MPEI products. The epoxy concentration was adjusted with the aim of controlling the thickness of epoxy layer. Figure 13 shows the SEM micrographs of the fractured MPEIs and the epoxy layer thickness variation as a function of epoxy concentration. It is seen that the epoxy layer was uniformly coated on the EPEI bead surface, and no obvious epoxy layer exfoliation was observed during sample bending. SEM micrographs with magnification of 2000× were used to further investigate the interface bonding and to calculate the epoxy layer thickness. It is found that the epoxy layers were almost stuck onto the bead foam’s surface and there was no observable gap between the

Figure 12. Schematic illustration of the compression molding process of the EPEI beads and MPEI specimens.

Figure 13. SEM micrographs of the fractured MPEIs and SEM micrographs illustrating the thickness of epoxy layer on PEI bead foams prepared by various epoxy concentrations.
foam’s surface and epoxy layer being observed. Meanwhile, no obvious epoxy was found within bubbles, resulting from the closed cell structure of the prepared EPEI bead. The epoxy thicknesses of EPEI beads with various epoxy concentrations were calculated, which were 1.9 μm (MPEI-1), 2.8 μm (MPEI-2), 8.3 μm (MPEI-3), and 10.1 μm (MPEI-4). Meanwhile, as shown in Table 2, the increased epoxy concentration caused the increased apparent density of MPEIs from 82.7 kg/m³ (MPEI-1) to 92.7 kg/m³ (MPEI-2), to 104.9 kg/m³ (MPEI-3), and to 116.9 kg/m³ (MPEI-4).

The foam density and properties of the MPEIs were manipulated by different compression degrees. The SEM images presented in Figure 14 show the fracture surfaces of MPEIs, where the epoxy concentration was 28.6%, and the compression degrees of 19.5, 23.2, 32.5, and 75.0% were applied. It is noted that the fracture mode of MPEIs was almost 100% intrabead fracture. This suggested that about 2.8 μm-thin epoxy layer was stronger than EPEI bead with a size of 5.0 mm. If not, the crack path would run through the bead boundaries. With the increase in compression degree, EPEI beads changed their shape and contacted more closely, resulting in the reduced voids among beads, which was consistent with the increased apparent density of MPEIs from 82.1 kg/m³ (MPEI-5) to 92.7 kg/m³ (MPEI-6), 118.4 kg/m³ (MPEI-7), and 218.3 kg/m³ (MPEI-8).

2.5. Properties of the MPEIs. It is well known that PEI resin exhibits excellent mechanical properties, intrinsic flame-retardant properties, and long-term service temperature of about 160–180 °C due to its high T_g of 220 °C. In this study, the ultralow-density EPEI beads with an expansion ratio of about 30–56 times were fabricated and then compression-molded into large-sized MPEIs using flame-retardant grade epoxy as an adhesive agent. In this section, we are going to investigate the mechanical, thermal stability, and flame-retardant properties of MPEI samples.

2.5.1. Tensile Properties. Figure 15 shows the tensile strain–stress curves of MPEI samples, where both the epoxy concentration and compression degree were adjusted. As shown in Figure 15A, MPEI-1 with an epoxy concentration of 22.2% has a tensile strength of 1.09 MPa and elongation at break of 4.75%. With increasing epoxy concentration, the tensile strength of MPEIs tends to increase gradually up to 1.92 MPa for MPEI-4 with an epoxy concentration of 66.7%. The epoxy concentration of 28.6% was fixed, and the compression degree was adjusted to change the tensile properties of MPEIs. As shown in Figure 15B, MPEI-5 with the lowest compression degree of 19.5% has a tensile strength of 0.75 MPa, and an increase in compression degree tends to increase the tensile strength dramatically up to 3.98 MPa for MPEI-7 with the compression degree of 75.0%. Meanwhile, the increased compression degree facilitated to increase the elongation at break gradually from 3.9% for MPEI-5 to 6.0% for MPEI-8.

Figure 16 summarizes the tensile strength of MPEIs as a function of apparent density. It is seen that the tensile strength of MPEI samples were linearly increased with both the epoxy concentration (black line) and compression degree (red line). Moreover, the slopes of the two fitting lines were the same, while the black line was on top of the red line. These results indicated that if the apparent density was the same, then the tensile strength of MPEIs obtained by changing the epoxy concentration would be a little bit higher than the ones expected.

**Table 2. Densities of MPEIs as a Function of Epoxy Concentration and Compression Degree**

| specimen | MPEI-1 | MPEI-2 | MPEI-3 | MPEI-4 |
|----------|--------|--------|--------|--------|
| epoxy concentration (wt %) | 22.2 | 28.6 | 40.0 | 66.7 |
| apparent density (kg/m³) | 82.7 | 92.7 | 104.9 | 116.9 |
| compression degree (%) | 19.5 | 23.2 | 32.5 | 75.0 |
| apparent density (kg/m³) | 82.1 | 92.7 | 118.4 | 218.3 |

Figure 14. SEM micrographs of the MPEIs prepared by changing the compression degree during the compression molding process.
prepared by changing the compression degree. This seems to suggest that the increase in epoxy concentration was more helpful in improving the tensile strength of MPEI samples.

We also compared the tensile properties of the available bead foam products, such as EPS, EPLA, EPP, and ETPU, with that of EPEI, and the results are summarized in Figure 17. EPS and EPLA have low tensile strength values of about 0.4 and 0.45 MPa, respectively, and the interface diffusion of amorphous chains generates the bonding among bead foams.7,45 EPP exhibits the obvious increased interbead bonding, especially for EPP15 (15 times bead foam expansion) with a tensile strength of 1.21 MPa, resulting from the occurrence of crystallization of the diffused polymer chains.44 ETPU has the further increased tensile strength of about 0.91–1.80 MPa,11 which is attributed to the diffusion of adequate amorphous chains as well as high foam density of about 240–350 kg/m³. Compared to the reported bead foams, EPEI exhibited the highest tensile strength, especially for MPEI-8 (foam density of 218.3 kg/m³) with a value of 3.98 MPa. It is believed that the strong epoxy layer among bead foams was the main reason for the formation of efficient interbead bonding.

2.5.2. Compression Properties. Compression behaviors are critical properties of bead foam products because of their applications. Figure 18 shows the compression stress–strain curves of MPEIs as a function of epoxy concentration. The linear elastic region is observed at the strain less than 5% for all four samples, where stress increases linearly with deformation and the strain is recoverable.11 With the increase in strain, a typical stress plateau region is presented, where the stress of MPEIs increases gradually with increasing strain. This phenomenon suggested that MPEIs exhibited a rigid characteristic under deformation, possibly resulting from the presence of rigid epoxy shell around EPEI beads.
obvious densification regions were observed on the curves, attributing to the presence of a large number of voids among EPEI beads. These voids were formed by a low compression degree during the compression molding process. As expected, an increase in foam density tended to increase the 50% compression strength from 1.36 MPa for MPEI-1 with a density of 82.7 kg/m³ up to 2.10 MPa for MPEI-4 with a density of 116.9 kg/m³.

2.5.3. Thermal Stability. The main limitation of current available bead foam products is their low service temperature and poor dimensional stability at high temperature. For example, EPS can only handle 80 °C because the T_g of PS matrix is about 100 °C. PP resin has the melting peak (T_m) of about 165 °C for homo-PP and of about 145 °C for PP copolymer. Therefore, the EPP product can remain stable at temperature less than 100–120 °C. In this study, the thermal stability of MPEIs at 160 °C for 48 h was investigated, where the square samples with a length/width of 100 mm and thickness of 20 mm were used. Table 3 shows the size shrinkage of molded EPEI samples after being thermally treated. As indicated in Table 3, the shrinkage of both length and thickness of the four MPEIs was about 0.0–0.1%, which demonstrated that MPEIs were quite stable under the test condition. Therefore, the newly developed MPEI foam could be potentially used at high service temperature.

2.5.4. Flame-Retardant Properties. Flame-retardant properties are of serious concern for foams used at aerospace, submarines, high-speed trains, and so on. PEI resin is well known for its excellent flame retardancy and less smoke generation. In this study, it is interesting to check the flame-retardant performance of the MPEI samples and figure out how the foaming process and epoxy coating affect the flame-retardant features of foams. Table 4 summarizes the LOI value, horizontal flammability rate, and melt dripping behavior of MPEIs. For comparison purpose, the properties of raw PEI and epoxy resin were also tested. As expected, PEI resin had a high LOI value of 47.0% and can also self-extinguish in air upward combustion, showing V0 rating in the UL-94 test. The LOI of the selected epoxy was about 32.0% and it showed V1 rating.

With the introduction of cell structure, the LOI of MPEI-1 reduced to 36.7%. It is well accepted that air can replace the blowing agent located in cells by aging. During the burning of foams, the increased air concentration in foams inevitably reduces the O₂ consumption, and the increased voids among polymers enhance the heat transfer from outside to inside and from inside to outside. It is a surprise to find that the increase in foam density tended to increase the LOI of MPEIs, which was 35.8% for MPEI-2, 34.2% for MPEI-3, and 32.1% for MPEI-4, respectively. As mentioned above, the four MPEIs had various epoxy concentrations, and the increase in MPEI’s density was caused by the increased epoxy content. Compared to PEI resin, the used epoxy had a lower LOI value and lower flame rating (i.e., V0 vs V1). Therefore, it is believed that the increased epoxy content was the main reason for the decreased LOI value and flame rating of MPEI-4. Both PEI resin and epoxy resin exhibited antidiamping properties, and the as-prepared MPEI samples also possessed excellent antidiamping performance.

3. CONCLUSIONS

The prepared microcellular foams based on high-performance polymer usually have a low expansion ratio less than 10 times due to the low gas solubility and rigid polymer matrix. In this study, acetone was selected as a co-blowing agent and compressed CO₂ as the blowing agent. Acetone exhibited high solubility of about 27.0% and 12.7% at room temperature and 60 °C, respectively. The acetone-soaked PEI beads were saturated by compressed CO₂, and the solubility of mixed fluid tended to decrease continuously with increasing CO₂ pressure due to the replacement of acetone by CO₂. Acetone has low diffusivity, which ensured the mixed fluid to be stored within the PEI matrix for more than 6 days.

A solid-state foaming process was conducted to foam PEI beads, and the prepared EPEI beads exhibited ultralow density with an expansion ratio of about 30~56 times and a microcellular structure with a cell density of 10⁷~10⁹ cells/cm³. The foaming temperature, saturation pressure, and desorption time were verified as critical parameters to affect the expansion ratio and cell morphology of EPEI beads. CO₂/acetone fluid reduced the matrix stiffness of PEI through a strong plasticization effect and supplied abundant gas for cell growth, which was thought as a crucial reason to obtain the EPEI beads with high volume expansion.

A novel compression molding process was carried out to prepare the MPEIs with epoxy as a coating agent. The good infiltration character of epoxy on EPEI beads induced the formation of strong interbed bonding among bead foams. Epoxy concentration and compression degree were two important parameters to control the mechanical properties of the MPEIs. Besides good mechanical properties, the MPEIs presented high dimensional stability at 160 °C and excellent flame-retardant properties, characterized by a high LOI value of 32.1~36.7% and V0 rating. These well-defined properties make the MPEIs very promising in many advanced applications.

4. EXPERIMENTAL PART

4.1. Materials and Preparation of the Solid Pellets. PEI (YZPI-JP10) was supplied by Nanjing Yuezi Chemical Ltd. According to the supplier, the PEI resin is amorphous with a glass transition temperature (T_g) of 220 °C. The
The chemical structure of PEI is shown in Scheme 1. CO₂ with a purity of 99.9% obtained from Ningbo Wanli Gas Corporation was used as the physical blowing agent. Acetone of reagent grade was obtained from Sinopharm Chemical Reagent Co., Ltd., and selected as the co-blowing agent for polymer foaming. A flame-retardant epoxy resin (HW-8329) was purchased from Shanghai Xrun Resin Co., Ltd. The PEI pellets were dried in the oven for 12 h at 150 °C before use. PEI beads with a diameter of 1.0−1.2 mm and aspect ratio of 1.2−1.5 were prepared by extrusion pelletization at a temperature of 340−350 °C. The PEI sheets with a thickness of 0.6 mm were obtained by compression molding at 350 °C, and the specimens with a size of 2.0 cm × 2.0 cm were cut for gas solubility measurement.

### 4.2. Gas Solubility Measurement

The CO₂ sorption behavior of PEI sheets was measured by a commonly accepted gravimetric method. The PEI sheets were placed in a high-pressure vessel with 500 mL volume at 60 °C. The vessel was flushed with compressed CO₂ for 1 min and then pressurized to 1−6 MPa. The saturation time was about 48 h to ensure an equilibrium adsorption of CO₂. After the CO₂ saturation process, the vessel was released and the sample was moved quickly from the vessel to a digital balance within 1 min to record the mass loss as a function of time. The mass uptake of CO₂ in the high-pressure vessel was calculated by linear extrapolation of the initial stage of the desorption curve of CO₂. The PEI sheets were soaked in liquid acetone at room temperature and atmospheric pressure for 2 weeks. The acetone sorption of PEI sheets was directly calculated based on the weight change of PEI sheet before and after acetone treatment. The acetone/CO₂ mixture sorption of PEI sheets was also measured by the gravimetric method, where the acetone-soaked PEI sheets were used for the CO₂ saturation for 48 h at 60 °C and 1−6 MPa. Additionally, 20 mL of acetone was put into the vessel during the CO₂ saturation process with the aim of controlling the acetone concentration within the PEI matrix.

The PEI beads were used to describe the evolution of the residual acetone/CO₂ within the PEI matrix as a function of desorption time. The percentage of residual acetone/CO₂ within PEI beads was calculated based on the weight change, and the desorption time was in a wide range of 1−144 h.

### 4.3. Solid-State Foaming

Solid-state foaming was carried out to foam the PEI beads and hot air was selected as the heating medium. The acetone-soaked PEI beads (200 g) together with acetone (20 mL) were placed in the high-pressure vessel (500 mL) with the treatment temperature of 60 °C. Then, the vessel was flushed with low-pressure CO₂ for about 1 min and then pressurized to 1−6 MPa. After the treatment of PEI beads for 48 h, the samples were removed from the vessel after a rapid quench of pressure (2 MPa/s) and transferred to a baking oven at 180−250 °C. The foamed samples were removed out of the oven after 60 s. In the case of PEI foaming using CO₂ and acetone, the saturation condition was 5 MPa/60 °C/48 h and 25 °C/2 weeks, respectively, and the same conditions were used during the foaming process.

### 4.4. Compression Molding of EPEI Beads

Epoxy and curing agent with a feed ratio of 1:1 were mixed with the diluting agent of acetone under the aid of vigorous stirring to get the epoxy adhesive. The EPEI beads were put into the epoxy adhesive and mixed using a glass rod. The epoxy-coated EPEI beads were rapidly transferred into a mold cavity that was connected with hot plates. The temperature of the hot plates was fixed to 120 °C. After filling, the EPEI beads were compressed with pressures of 2−10 MPa until the occurrence of epoxy curing completely. The epoxy layers solidified and then generated strong interlayer bonding among bead foams. The epoxy concentration and compression degree were adjusted to control the interlayer bonding strength and the density of the MPEIs. The compression degree (CD) was calculated using eq 1 as follows

$$\text{CD} = \frac{V_0 - V_1}{V_0} \times 100\% \quad (1)$$

where $V_0$ is the volume of filled EPEI beads and $V_1$ is the volume of MPEIs.

### 4.5. Characterizations

The densities of PEI bead ($\rho$) and foamed PEI beads ($\rho_f$) were measured via the water displacement method in accordance with ASTM D792, and the apparent density of the MPEI samples ($\rho_{app}$) was measured based on ASTM 1895. $\phi$ is the volume expansion ratio of the polymer foam, which can be calculated using eq 2 as follows

$$\phi = \frac{\rho}{\rho_f} \quad (2)$$

The morphology of the foamed samples was observed with a Hitachi TM-1000 scanning electron microscope. The samples were freeze-fractured in liquid nitrogen and sputter-coated with gold. Both cell size and cell density were determined from the SEM micrographs. The cell diameter was the average of sizes of at least 100 cells on the SEM micrographs. The cell density ($N_0$), the number of cells per cubic centimeter of solid polymer, was determined using eq 3 as follows

$$N_0 = \left(\frac{nM^2}{A}\right)^{3/2} \phi \quad (3)$$

where $n$ is the number of cells in the SEM micrograph, $M$ is the magnification factor, and $A$ is the area of the micrograph (in cm²).

Rectangular and circular specimens were prepared from the MPEI samples for the tensile and compression tests. The typical dimensions of the specimens for tensile test were as follows: thickness, 20 mm; width, 25 mm; length, 120 mm. The dimensions for the compression tests were as follows: diameter, 100 mm; thickness, 20 mm. Tensile strength testing was carried out according to ASTM C393-00 on an Instron 5567 testing machine at a crosshead speed of 10 mm/min, and compression strength testing was carried out based on ASTM365-03 with a crosshead speed of 2 mm/min. At least five specimens were tested under each condition, and the average value was used in this paper.

Square specimens with a length and width of 100 mm and thickness of 20 mm were prepared from the MPEI samples for the thermal stability test. The dimensional stability of molded...
EPEI was conducted at 160 °C for 48 h based on GB/T 8811-2008. Shrinkage (S) was calculated using eq 4 as follows

\[ S = \frac{L_0 - L_1}{L_0} \times 100\% \]  

where \( L_0 \) is the original size of MPEIs and \( L_1 \) is the sample size after being thermally treated at 160 °C for 48 h.

The LOI measurement (Vouch 5801A, according to ASTM D2863) and UL-94 vertical burning test (Vouch 5402, according to ASTM D3801) were used to characterize the flame retardancy of all samples. The test samples for LOI and UL-94 were 130 × 10 × 10 and 127 × 12.7 × 13 mm³, respectively. The LOI values of the MPEIs were measured by using an oxygen index meter (JF-3) produced by Jiangning Analysis Instrument Factory, China.

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### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors are grateful to the National Natural Science Foundation of China (grants 51573202 and 51873226) for the financial support of this study.

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