The fabrication and characterization of polymeric microcellular foams with designed gradient density

Qiang Shen, Yuanlu Xiong, Huan Yuan, Guoqiang Luo*, Xue Liang, Lianmeng Zhang
State Key Laboratory of Advanced Technology for Materials Synthesis and Processing,Wuhan University of Technology, Wuhan 430070, P.R. China
E-mail: luoguoqiang1980@sina.com

Abstract. The fabrication of polymeric foams with gradient density is a key to investigate the response of materials in quasi-isentropic loading. In this work, a non-traditional approach was proposed to fabricate the polymeric foam monolayer with designed density in a fixed volume by using the pre-mixture of expandable and expanded polymeric microballoons. After heating, the expandable microballoons expanded and bonded together to be integrated block with the final density from 0.1 g/cm³ to 0.5 g/cm³. The gradient density foams were fabricated by bonding with different monolayer. The microstructure and mechanical properties of each layer were investigated by SEM and compression strength tests. The results showed that the density of polymeric foams was matched with the design value very well by controlling the ratio of expandable and expanded polymeric microballoons. The uniform closed-cell structure with good bonding interface was shown from the SEM picture. And the mean cell size is less than 35μm. The polymeric foams exhibited ideal compressive behavior with the compressive strength as high as 9MPa. The Young’s modulus and compressive strength nearly linear increased with the increasing of density. The extremely wide range of accessible densities should make this technology for broad application prospects.

1. Introduction
The quasi-isentropic compression technique has been an important way for measuring material’s properties at high pressure, due to the accompanying temperature rise is much less severe than during shock-loading experiments [1,2]. It always used a density gradient material with increasing shock impedance away from the target material with light gas-gun [3,4]. This density gradient material is called impactor. The ideal impactor requires the densities ranging from 0.1 g/cm³ to 15 g/cm³ over a space of several millimeters [5]. The density gradient impactor under high and medium density region has been prepared successfully by tape casting method with different metal powder mixtures [2,6]. However, the impactor with low density region (from 0.1 g/cm³ to 1.2 g/cm³) is still hard to prepare by the same techniques.

The low density gradient material is usually composed with polymeric foams by stacking with different foam monolayer slices. Chen [7] has fabricated a multi-layer gradient foams material with the density range from 0.5 g/cm³ to 1.0 g/cm³ by stacking six epoxy resin foam monolayer together. Much lower density layer can not be made using the same preparation technique of mixing the epoxy resin matrix with plastic microballoons. Chemical or physical foaming method can easily prepare polymeric foams with much lower density [8]. However, it is hard to control the products with designed density due to the uncontrollable foaming speed. And the monolayer slices with required shape (less than 1mm) are difficult to process.
successfully by such a low density and large cell size foam block.

In order to fabricate the low density foam monolayer with designed density, a non-traditional approach was proposed to fabricate the polymeric foams in a fixed volume by using the pre-mixture of expandable and expanded polymeric microballoons together. After heating, it allows only expansion of the expandable powder to fill the interstices between the expanded microballoons [9,10]. The real density, microstructure and mechanical properties of the polymeric foams were investigated.

2. Experimental

The expandable microballoons (F-30D) and the expanded microballoons (FN-80SDE) were both purchased from Matsumoto Yushi-Seiyaku Co., Ltd., Japan. SEM images of the expandable powder and expanded powder are shown in Figure 1. The particle size of expandable microballoons is 10–20 μm, and the expanded microballoons is 20–40 μm. The packing density of F-30D and FN-80SDE was calculated by measuring the mass of the powder and the real volume occupied by the powder in a 100 ml graduated cylinder after tapping 50 times on the counter.

![Figure 1](a) expandable and (b) expanded microballoons

The expandable and expanded polymeric microballoons were mixed homogeneously together at a ratio such that the tap density of the mixed powder was the same as the final density of the foams. The designed density of each foam monolayers is varied from 0.1 g/cm³ to 0.5 g/cm³. After completely filling the mixed powder into the fixed volume mold, it was heated to 155 °C for 30 minutes in the oven. Therefore, the expandable microballoons expanded and bonded together as integrated foams. The schematic diagram is shown in Figure 2. The fixed volume is about 50 mm × 1 mm for the preparation of monolayer slices. After
totally cooling down, the sample was demoded. The real density was obtained by measuring the volume and weight of different monolayer. Samples were freeze fractured in liquid nitrogen and the fracture surface was sputter-coated with gold before SEM test. For mechanical strength test, the sample was fabricated in another mold with a fixed volume of $\phi 20\text{mm} \times 16\text{mm}$.

3. Results and discussion

Results show that the packing density is 0.5050 g/cm$^3$ for expandable microballoons and 0.0086 g/cm$^3$ for expanded microballoons respectively. In a fixed volume, the design density is determined by the weight ratio between expandable and expanded microballoons. Figure 3 shows the tested densities and theoretical densities of the foams. The density decreased as the weight fraction of expanded powder increased. And the experimental data is very close to the theoretical value. It illustrates that the density of the polymeric foams is able to be controlled precisely by this fixed volume foaming method.

![Figure 3](image)

**Figure 3** Tested and theoretical density value of monolayer at composition of different weight fraction of expanded powder

Figure 4 shows the SEM images of fracture surfaces of monolayer foam with different magnification and different density. It can be seen that the polymeric foams has a very smooth surface and neat shape with the thickness of 1mm. Much thinner monolayer can be obtained by adjusting the thickness of the fixed volume mold. So the density gradient foams could be easily prepared by tacking several monolayer slices together with epoxy resin as bonder. From the high magnification images shown in Figure 4(b) and (d), it is clear that the nice uniform closed-cell structure with the pore size less than 35 $\mu\text{m}$ was gotten. The polymeric foam with higher density has much smaller pore size. And the pore structure tended to deformed shown in Figure 4(c). It attributes to the expandable powder compete to grow up under heating. When the density of the foam was low, the pore structure can grow freely and leads a larger pore size in such a fixed volume which was shown in Figure 5(e).
In addition, the foams show a very perfect bonding interface which implies the excellent mechanical properties according to the figure 4(c) and (d). Actually, those microballoons contain vinyl chloride which provides an activated shell surface. When the heating temperature is higher than the initial softening temperature (about 80–85°C for F-30D), the expandable microballoons will grow bigger and bigger due to the gasification phenomenon of the inside volatiles [11,12]. The shell surface is bonded together finally to be a foam block.

Figure 5(a) shows the compressive stress-strain curves of foams as a function of density varied from 0.1 to 0.5 g/cm$^3$, respectively. The typically linear regime and plateau regime of the stress-strain curves are very clear. The plateau stress is nearly constant during the plastic plateau regime which illustrates that the foam products exhibited nearly ideal compressive behavior. Figure 5(b) shows the change of Young’s modulus and compressive strength as a function of density. The compressive strength can achieve as high as 9MPa when the density is about 0.5 g/cm$^3$. Both the Young’s modulus and the compressive strength decreased linearly with the decreasing of density.
4. Conclusion
The foam monolayer slices with designed density could be fabricated by using the pre-mixture of expandable and expanded polymeric microballoons in a fixed volume mode under heating. The density can be controlled precisely varied from 0.1 to 0.5 g/cm³. The cell size is less than 35μm. And it has a very perfect bonding interface which promotes the compressive strength up to 9 MPa. This work offers a simple method to get the low density gradient material by stacking monolayer slices with different fixed density.

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