Study on mechanical properties of epoxy-fly ash cenosphere syntactic foams

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Abstract. Epoxy syntactic foams (ESFs) with different fly ash cenospheres (FAC) were fabricated by stirring cast method. The compressive properties and energy absorption characteristics of the epoxy resin (EP) and the ESFs were investigated under the quasi-static compression. The failure mechanism and fracture morphology of ESFs were analyzed using scanning electron microscope (SEM). The results show that the compressive strength and modulus of ESFs increased firstly and then decreased with the increase of FAC contents. The main failure mechanism of ESFs have the brittle fracture of EP, the fracture and crushed of FAC and debonding of EP/FAC interface.

1. Introduction

Epoxy resin is one of the commercial materials with many excellent properties such as low density, high stability, and good corrosion resistance [1-3]. And it is often widely used in aviation, aerospace, construction and chemical fields [1,4]. However, EP is associated with brittleness, poor stress cracking resistance, low impact strength and insufficient fatigue resistance [5,6]. Therefore, in order to overcome these disadvantages, it is necessary to modify the epoxy resin.

EP modification has attracted wide attention of some researchers, and most of them think that EP with filled inorganic particles is beneficial to improving the toughness. ESFs are consist of EP and hollow microballoons, and they have many excellent properties, such as low density, high specific strength, and excellent energy dissipation capacity [7-9]. Swetha et al investigated the compressive behaviour of hollow glass microspheres/epoxy based syntactic foams under the quasi-static compressive condition, and the results showed the strength decreases of these foams with increase in hollow spheres content [7]. Nikhil et al found that the compressive strength and modulus of functionally graded syntactic foams can be increased by choosing microballoons of higher thickness [8]. Li P et al reported the strain rate dependent compressive properties of glass microballoon epoxy syntactic foams, and proved the strength of epoxy matrix increases with increasing strain rate [9].

Recently, another kind of hollow microballoon, i.e. fly ash cenosphere (FAC) was used to fabricate epoxy syntactic foams. The FAC is the by-product during the combustion of coal in thermal power plants. However, it has lots of amazing properties, such as low density, low cost and excellent heat resistance that make them amenable to a wide range of applications [10-14]. Proper utilization of FAC will not only conserve resources but also benefits the environment [11,15].

Therefore, in this study, EP-FAC ESFs with different contents of FAC were fabricated. The compressive properties and energy absorption characteristic of the ESFs were investigated.
2. Experimental procedure

2.1 Preparation of Materials

The size of FAC is at a level of ~100 μm. The density of the FAC was about 0.3-0.6 g/cm³. The chemical compositions of FAC were listed in Table 1.

| Composition | SiO₂ | Al₂O₃ | Fe₂O₃ | SO₃ | CaO | MgO | K₂O | Na₂O | TiO₂ |
|-------------|------|-------|-------|-----|-----|-----|-----|------|------|
| Contents    | 50-65| 25-35 | 2-4   | 0.1-0.2 | 0.2-0.4 | 0.8-1.2 | 0.5-1.1 | 0.3-0.9 | 0.5-3 |

Firstly, the FAC was dried at 120°C for 2h. The liquid bisphenol-A epoxy resin was stirred and the FAC with the different mass fractions of 2%, 4% and 6% were filled with the dilute resin. Then, the defoaming agent was added into the dilute liquid. Afterwards, the aliphatic amine was poured and stirred to reach maximum dilute and uniform mixing. Finally, the uniform mixing liquid was oscillation with assistant of ultrasonic vibration. The curing process was carried under a low negative pressure to remove air bubble from the materials.

2.2 Compressive test

The compressive tests were carried out using an MTS universal testing machine at room temperature. The compressive tests were employed at a nominal strain rate of ~10⁻³/s. The stress-strain curve was calculated by experimental data from load-displacement curves.

The compressive strength of the material is defined as the first peak stress in the stress-strain curve. The compressive modulus is determined by the slope of linear elastic region in the stress-strain curve. The energy absorption capacity of the material, W, can be evaluated from the stress-strain curve by using the following equation [16]:

$$ W = \int_{0}^{\varepsilon} \sigma d\varepsilon $$  \hspace{1cm} (1)

where $\varepsilon$ is the compressive strain and $\sigma$ is the compressive stress.

The energy absorption efficiency, I, can be calculated using the following equation [16]:

$$ I = \frac{1}{\sigma_{\text{max}}} \int_{0}^{\varepsilon} \sigma d\varepsilon $$  \hspace{1cm} (2)

where, $\sigma_{\text{max}}$ is the maximal stress as the strain ranging from 0 to $\varepsilon$ in the stress-strain curve.

2.3 Characterization

The microstructures of the materials were analyzed by scanning electron microscopy (SEM, Model JSM-5310, JEOL, Japan and Model EVO18 ZEISS, Germany). The phase compositions of the FAC were analyzed by X-ray diffractometer (DX-2007, China). The radiation source is Cu Kα. The scanning angular scope is from 20° to 80°, and the scanning speed is 4°/s.

3. Results and discussions

3.1 Characterization of FAC

Figure 1(a) shows the SEM image of FAC. It is clear that the FAC is spherical shape. The size distribution of the FAC is shown in figure 1(b). The average size of FAC is about 102.73 μm.
Figure 1. SEM image and size distribution of FACs.

Figure 2(a) and (b) show the eternal and inner SEM image of the FAC, respectively. The eternal of FAC is approximately smooth, but still has few defects. The FAC is hollow and its shell wall contains some micro-pores. The thickness distribution of shell wall of the FAC is shown in figure 2(c). The average thickness of shell wall is about 5.37 μm.

Figure 2. SEM image and the thickness distribution of shell wall of the FAC.

3.2 Microstructure of epoxy syntactic foams and the XRD analysis of FAC

Figure 3 shows the XRD pattern of the FAC. It can be seen that the as-received FAC mainly contains Al₂O₃ and SiO₂ phase. Figure 4 shows the SEM image of epoxy syntactic foams. It can be seen from figure 4(a) that the FAC are uniformly distributed in the EP, which is beneficial to the mechanical properties of epoxy syntactic foams. Figure 4(b) shows that the interface between FAC and the EP is well bonded, and there is no crack and micro-pore in the interface. Besides, it also display the inner and thickness of FAC.

Figure 3. The XRD pattern of FAC. Figure 4. SEM images of epoxy syntactic foams.

3.3 The compressive properties of the ESFs

Figure 5(a) shows the compressive stress-strain curves of the ESFs with different contents. It can be seen that the curves contain three typical regions: linear elastic region, plateau region and densification
region. The curves represent a peak when the strain is around 0.05, and then the stress value exhibits a drop, indicating that the crack appears in EP. The stress drops again when the strain is about 0.45, but it can be seen clearly that the degree of drop decreases with increasing contents. Table 2 shows the compressive strength and modulus of ESFs. And the energy absorption and energy absorption efficiency was calculated at the strain of 0.5. From figure 5(a) and table 2, it can be seen that the compressive strength and modulus increases firstly and then decrease with the increase of FAC contents. Compared with the neat EP, the highest increase of the compressive strength (11.8%) and modulus (19.3%) were obtained when the content of FAC was 2 wt%. It can also be seen from figure 5(c) that the ESFs with 6 wt% have a highest energy absorption efficiency when strain from 0.05 to 0.5 compared to other contents, and the highest value is 0.84 at the strain of 0.35, which is mainly due to a long and smooth plateau region. To further get insight to the deformation mechanism of ESFs, the failure morphology were observed.

Figure 5. The compressive properties of ESFs with different FAC contents: (a) compressive stress strain curves; (b) energy absorption; and (c) energy absorption efficiency.

| FAC contents | Compressive Strength/MPa | Compressive Modulus/MPa | Energy absorption/(MJ/m³) | Energy absorption efficiency |
|--------------|--------------------------|-------------------------|---------------------------|-----------------------------|
| 0%           | 71.76                    | 1231                    | 41.34                     | 0.63                        |
| 2%           | 80.25                    | 1468                    | 40.58                     | 0.69                        |
| 4%           | 73.63                    | 1439                    | 34.83                     | 0.78                        |
| 6%           | 68.61                    | 1315                    | 35.52                     | 0.80                        |

3.4 The failure mechanism of the ESFs

Figure 6 shows that the failure mechanism of ESFs. It can be seen from figure 6 (a) that there are many broken and fracture microballoons and some smooth fracture surface and crack appear around the FAC. Figure 6 (b) display a serial of crack propagation and a large cleavage plane, so it shows a characteristic of brittle materials. Crack propagation is interrupted when across the FAC, so FAC play an important role in resisting crack propagation and FAC is beneficial to reducing the brittle of materials. Figure 6 (c) and figure 6 (d) exhibit that the fracture surface include rough and smooth morphology, and there are some FAC chips on the surface, and the debonding interface is also observed. Figure 6 (e) and figure 6 (f) show the fracture morphology when strain reaches to 0.6, it clearly represents that there is no hollow cenosphere because of the crashing and crushing of FAC. In summary, the fracture of ESFs include the brittle fracture of epoxy resin, the debonding and crushing of FAC, and resisting crack propagation of FAC.
4. Conclusions
In this paper, the epoxy syntactic foams were fabricated by stirring cast method. The conclusions can be drawn as following:

1) All the stress-strain curves of the materials contain three regions: linear elastic region, plateau region and densification region. The compressive strength and modulus of ESFs increased firstly and then decreased with the increase of FAC contents. The FAC can reduce the fluctuate of stress-strain curves.

2) The highest values of compressive strength and modulus are 80.25MPa and 1468MPa, increasing 11.8% and 19.3% compared to neat EP. And the highest energy absorption efficiency value is 0.84 when the content of FAC is 6wt%.

3) The failure mechanism of ESFs are multiple, including the brittle fracture of epoxy resin, the debonding interface between EP/FAC and crushing of FAC. In addition, the FAC could resist the crack propagation in the EP.

Reference
[1] Chen P, Li JC, Zhang L. (2018) Analysis of mechanical characteristics of fly ash cenospheres reinforced epoxy composites. J Wuhan Univ Technol, 33: 139-45.
[2] He HW, Li KX, Wang J, et al. (2011) Study on thermal and mechanical properties of nano-calcium carbonate/epoxy composites. Mater. Des., 32: 4521-7.
[3] Sun T, Fan HY, Wang Z, et al. (2015) Modified nano Fe₃O₃ epoxy composite with enhanced mechanical properties. Mater. Des., 87: 10-6.
[4] Kang YK, Chen XH, Song SY, et al. (2012) Friction and wear behavior of nanosilica-filled epoxy resin composite coating. Appl. Surf. Sci., 258: 6384-6390.
[5] Sprenger S. (2013) Epoxy resins modified with elastomers and surface-modified silica nanoparticles. Polym., 54: 4790-4797.
[6] Liu SL, Fan XS, He CB. (2016) Improving the fracture toughness of epoxy with nanosilica rubber core shell nanoparticles. Compos. Sci. Technol., 125: 132-140.
[7] Swetha C, Kumar R. (2011) Quasi-static uni-axial compression behaviour of hollow glass microspheres/epoxy based syntactic foams. Mater. Des., 32: 4152- 4163.
[8] Nikhil G, William R. (2006) Comparison of compressive properties of layered syntactic foams having gradient in microballoon volume fraction and wall thickness. Mater. Sci. Eng. A, 427: 331-342.
[9] Li P, Petrinic N, Siviour CR, Froud R, Reed JM. (2009) Strain rate dependent compressive properties of glass microballoon epoxy syntactic foams. Mater. Sci. Eng. A, 515: 19-25.
[10] Gu J, Wu GH, Zhao X. (2009) Effect of surface-modification on the dynamic behaviors of fly ash cenospheres filled epoxy composites. Polym., 30: 232-238.

[11] Ahmaruzzaman M. (2010) A review on the utilization of fly ash. Prog. Energ. Combust., 36: 327-363.

[12] Juang SWH, Xue CS. (2015) Investigation of mechanical properties and microstructures of aluminum-fly ash composite processed by friction stirring. Mater. Sci. Eng. A, 640: 314-319.

[13] Rajan TPD, Pillai RM, Pai BC, et al. (2007) Fabrication and characterisation of Al-7Si-0.35Mg/fly ash metal matrix composites processed by different stir casting routes. Compos. Sci. Technol., 67: 3369-3377.

[14] Gu J, Wu GH, Zhang Q. (2007) Effect of porosity on the damping properties of modified epoxy composites filled with fly ash. Scripta Mater., 57: 529-532.

[15] Dilip CD, Sri B, John R, et al. (2011) Study of dynamic mechanical properties and morphological behaviours of fly ash reinforced polypropylene composites. Macromol. Res., 19: 338-344.

[16] Banhart J. (2001) Manufacture, characterisation and application of cellular metals and metal foams. Prog. Mater. Sci., 46: 559-632.