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Synthesis and properties of the vapour-grown carbon nanofiber/epoxy shape memory and conductive foams prepared via latex technology

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ABSTRACT

Vapour-grown carbon nanofiber (VGCNF)/epoxy foams were prepared via latex technology. VGCNFs were first dispersed in water-borne epoxy resin by intensive stirring and then mixed with curing agent and blowing agent at room temperature. VGCNF/epoxy foams were obtained from these mixtures via freeze-drying and foaming under a vacuum at 100 °C. The shape memory properties of the epoxy foams were evaluated together with other physical properties. Compression and thermo-mechanical cycle tests were performed to measure the effects of the VGCNFs on the mechanical performance of the foams. Electrical conductivity was measured using a standard four-point method. The experimental results indicated that the VGCNF/epoxy foams had a low glass transition temperature of 48 °C, resulting in a fast recovery rate at 65 °C in 10 s. The epoxy foam had a high shape recovery and fixity ratio of more than 90% after several thermo-mechanical cycles with the addition of 1.0 wt% VGCNFs. The VGCNFs enhanced the strength and electrical conductivity of the epoxy foams. The percolation threshold for conduction was approximately 0.6 wt% of VGCNFs in the composites. Moreover, the electrical conductivity of the improved epoxy foam did not significantly decrease with increasing thermo-mechanical cycles below 80% compression strain.

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1. Introduction

Shape memory polymer (SMP) foams are attracting considerable interest worldwide [1–3]. SMP foams possess low density, high compressibility, and shape memory (SM) behaviour. Thus, these foams have potential use in a wide range of applications that require a material to expand from a packaged shape to a much larger shape with minimal out-of-plane shape change [4–8]. SMP foams are also advantageous for applications that require extremely high volume recovery ratios. For example, SMP foams can be used as actuators that can be packaged on earth and recovered in space [9], thereby conserving the carried volume. Thus, SMP foams can also be used as a scaffold for cellular in-growth and combined with biological agents to promote biological integration [10,11]. SMP foams are ideal candidates for multifunctional devices.

For heat-activated SMP foams, the SM effect is observed by performing a typical thermo-mechanical cycle. These foams are rigid below their glass transition temperature (T_g), and become spongy when heated above T_g . In this state, the foams can be packed into completely collapsed pores, without generating significant divided into categories based on their chemical nature; the most common categories are polyurethane-based [12-14], polystyrene-based [15,16], and epoxy-based [17,18] foams. Epoxy resins, which are widely used in several non-SM applications, such as coatings, adhesives, construction, and manufacturing, exhibit the desirable properties of high strength, and good thermal stability. and chemical resistance. Conferring SM properties to these versatile resins has been the subject of several researchers, leading to some advances in the development of SM epoxy resin. Recent studies have shown the good SM properties of epoxies [9,19]. Furthermore, SM epoxy has superior environmental durability, and is a good candidate for space application. Squeo and Quadrini [20] developed a new foaming technology for epoxies, namely, "solidstate foaming", which can produce foams without using any blowing agent or liquid-state process. The solid-state epoxy foams exhibit good SM properties. This new kind of material has been applied to the actuators of the International Space Station [9]. However, the solid-state foaming technique is only applicable only in solid epoxy resins, not in liquid epoxy resins.

damage. This compact structure remains stable without constraining force, when cooled below T_g . When heated above T_g , the foams

recover their original shape. Heat-activated SMP foams can be

In the present study, the latex technology was used to prepare vapour-grown carbon nanofiber (VGCNF)/epoxy foams. VGCNFs

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are used to enhance the strength, stiffness, and electrical conductivity of epoxy foams. The SM properties and electrical conductivity of the VGCNF/epoxy foams are evaluated. The advantages of this technique include simplicity, versatility, reproducibility, and reliability. This study is the first to report this new method of preparing SM epoxy foams from water-borne epoxy resin via the latex technology.

2. Materials and methods

2.1. Materials

VGCNFs (VGNF[®], Showa Denko K.K., Japan) were fabricated via thermo-chemical vapour deposition. The commercially available epoxy resin (diglycidyl ether of bisphenol A) E-44 (epoxy equivalent ~ 213–244) was supplied by the Wuxi Resin Factory, China. The surfactant for epoxy emulsion is a new reactive copolymer epoxy-toluene diisocyanate-Triton X-100 (EP-TDI-TX100), which has been successfully synthesized in our previous research [21]. A room-temperature cuing agent was obtained from Zhejiang Anbang New Material Development Co., Ltd. The blowing agent used was a tertiary butanol obtained from commercial sources. All experiments were performed using deionized (DI) water.

2.2. Preparation of water-borne epoxy resin

The water-borne epoxy resin used was synthesized from EP/EP-TDI-TX100 emulsion using the phase-inversion technique. The surfactant EP-TDI-TX100 (20 g) and epoxy resin (180 g) were added into a 500 mL three necked-flask, warmed to 70 °C, and stirred to homogeneity. The mixture was then poured into a 1500 mL stainless steel cup and stirred at 10 °C using an ice bath maintain a low emulsification temperature. The shearing speed was 3000 r/min. DI water was added dropwise until phase inversion occurred. Enough water was added to produce a water-borne epoxy resin with 50% solid weight.

2.3. Preparation of VGCNF/epoxy SMP foams

A three-step procedure was used to prepare the epoxy foams. First, VGCNFs were added to a beaker with water-borne epoxy resin and dispersed to homogeneity at room temperature using an intensive mixer. The blowing agent tertiary butanol (2.5 wt% of the mixture) and the curing agent (AB-HGA) were then sequentially added to the mixture. The weight ratio of the water-borne epoxy resin to the cuing agent was 4:1. Second, the mixture was frozen in liquid nitrogen for 5 min, and the aqueous solvent was removed using a Labconco Free Zone freeze-dryer operated at 0.1 mbar and -20 °C for 48 h. The resulting powder was shaped via cold compaction in a 5 mm tall and 40 mm wide stainless steel mould at a packing pressure of 5 MPa for a holding time of 5 min. Third, the foaming process was performed by placing a single tablet in a 40 mm wide cylindrical stainless steel mould. The epoxy tablets were foamed in a vacuum oven at 100 $^\circ$ C and -0.1 MPa for 48 h.

2.4. Transmission electron microscopy (TEM)

The TEM dispersion states of the water-borne epoxy resin were examined using a transmission electron microscope (JEM-2100F, JEOL, Japan) operated at 200 kV. The epoxy emulsion was diluted 10-fold and deposited onto the carbon-coated copper grids by drop-casting. The sample was then dried in vacuum for TEM observation.

2.5. Scanning electron microscopy (SEM)

SEM observations of the specimens before and after compression were conducted using a field emission scanning electron microscope (Ultra 55, Zeiss, Germany) at an operating voltage of 3 kV. Prior to testing, the samples were sputter-coated with gold to impart electrical conductivity and reduce charging artefacts. High vacuum conditions were applied and a secondary electron detector was used for image acquisition.

2.6. Compression test

A compression test was conducted flat-wise, based on ASTM C 365 using a universal testing machine (INSTRON 8531) to evaluate the mechanical properties of the prepared foam. The specimens were polished to a size of 25 mm \times 25 mm \times 12.5 mm, and then tested. The loading rate was 1.3 mm/min at room temperature. A preload of 0.2 N was used to achieve full contact of the plate on the sample. At least five effective specimens were tested.

2.7. Electrical conductivity measurements

The electrical conductivities of the VGCNF/epoxy foam before and after the thermo-mechanical cycles were determined. For four-point measurements, the flat surfaces of the foam samples were firmly pasted with conductive coating around their circumference at a spacing of approximately 1 mm. Conductive coating leads were attached to these electrodes for testing.

2.8. Dynamic mechanical analysis (DMA)

The foam specimens were determined using a DMA Q800 (TA Instrument, America) at a frequency of 1 Hz and heated from -30 °C to 145 °C at a rate of 5 °C/min. The test was run under engineering strain control, with a strain of 0.1% and a preload of 0.01 N. The ends of the samples were wrapped with aluminium foil to avoid the fracture in the grips.

2.9. Thermo-mechanical cycle test

A thermo-mechanical cycle test was conducted to investigate the shape recovery property of the epoxy foams. The specimens were compressed to the maximum strain of 80% (ε_m) at a constant compression speed at 65 °C above T_g (step 1). Maintaining the strain at 80%, the specimen was cooled down to 25 °C below T_g (at the glass state) and held for 10 min (step 2). The specimen was unloaded at 25 °C at a small unloading strain ε_u (step 3), completing the three-step shape fixity process. The specimen was heated from 25 °C to 65 °C without load and held for 10 min to examine the shape recovery capacity. The strain of the specimen was then recovered. When this cycle finished, a residual strain remained. The heating or cooling speed was 5 °C/min, and the loading and unloading speed was 1.3 mm/min. The test was repeated four times.

3. Results and discussion

3.1. Water-borne epoxy resin

Fig. 1 shows the SEM and TEM images of the water-borne epoxy resin particles. The particle size analysis (Delsa Nano C, Beckman Coulter, USA) determined an average particle diameter of 137 nm, with particles ranging from 50 nm to 300 nm (see the inset picture of Fig. 1A).



Fig. 1. (A) SEM micrograph of the water-borne epoxy resin particles. The sample was frozen in liquid nitrogen, and the aqueous solvent was removed using a Labconco FreeZone freeze-dryer operated at 0.1 mbar and -20 °C for 48 h. Scale bars: 200 nm. The inset shows the particle size distribution for the water-borne epoxy resin; and (B) TEM micrograph of the water-borne epoxy resin particles.



Fig. 2. (A) Micrograph of the epoxy foam; and (B) the average cell diameter distribution.



Fig. 3. Electrical conductivity of the VGCNF/epoxy foams as a function of VGCNF concentration.

3.2. Epoxy foam micrograph

The microstructures of the epoxy foam are shown in Fig. 2A. The SEM image shows that the cells with a diameter up of to $650 \,\mu\text{m}$ were evenly distributed in the epoxy resin. Furthermore, the shape of the cells is polyhedral rather than spherical because of the compression among the cells. The epoxy foam density was dependent on the blowing agent (tertiary butanol) content. At the end of the production stage, the epoxy foam density was approximately 0.29 g/cm³. The maximum (Max_d) and minimum diameter (Min_d)



Fig. 4. High magnification micrograph of the VGCNFs in the cross-section of the cell wall of the VGCNF/epoxy foam.

of every cell in Fig. 2A was measured using the ImageJ imaging processing software. The average cell diameter distribution of the $[(Max_d + Min_d)/2]$ is illustrated in Fig. 2B.

3.3. Electrical conductivity of the VGCNF/epoxy foams

Fig. 3 shows the effect of VGCNF concentration on the electrical conductivity of the VGCNF/epoxy foams. The electrical conductivity of the foam significantly increased when the VGCNF content



Fig. 5. (A) Compressive stress-strain curves of the epoxy foam; and (B) stress-strain response of the epoxy and VGCNF/epoxy foams at room temperature.

is approximately 0.6 wt%, indicating that the percolation threshold for the formation of a conductive VGCNF network in the epoxy matrix is achieved. The conductivity of pure water-borne epoxy resin is in the order of 10^{-13} S/m. For a VGCNF concentration of 1.0 wt%, the conductivity is 10^{-3} S/m. For higher VGCNF concentrations, no pronounced increase in conductivity could be observed. VGCNFs are excellent and favourable fillers for synthesising conductive polymer composites because of their high electrical conductivity, which can remarkably decrease the electrical resistivity of the composite at low weight or volume content. The significant increase in the electrical conductivity and uniform distribution of VGCNFs in the cell wall of the epoxy foam, as shown in Fig. 4.

3.4. Compression results

Fig. 5A shows the compressive stress–strain curve of the epoxy foam, which exhibits similar regimes to the stress–strain curve of regular syntactic foams. The stress–strain curve can be clearly characterised by three distinct regions. In the initial elastic regime and during early yield, the stress almost linearly increases as the foam becomes rigid. Subsequently, a wide plateau region corresponding to the rubbery deformation of the foam matrix is observed. In the end, the cell collapses and becomes compact with further increase in strain, and the stress–strain curve is directed upward *t* towards higher stress, at a larger strain. Compared with regular syntactic foam, the deformation in the rubbery region is obviously much higher [16,18]. This finding suggests that the foam can absorb more energy without disintegration. Furthermore, the 10 s free shape recovery rate of the epoxy foam at 65 °C is 94.5% at 93.35% pre-deformation strain.

The compression test results of the epoxy and VGCNF/epoxy foams are shown Fig. 5B. The strengths of the VGCNF/epoxy foams at 80% deformation strain were higher than that of the pure epoxy foam. The foam strength initially increases with the weight fraction of VGCNF and then decreases when the weight fraction reaches 0.8 (inset in Fig. 5B). The mechanical behaviour of the VGCNF/epoxy foam improved with respect to the unreinforced foam.

3.5. DMA results

The storage modulus and tan delta of the epoxy and 1.0 wt% VGCNF/epoxy foams from the DMA test are shown in Fig. 6. The T_g of the VGCNF/epoxy foam is approximately 48 °C lower than that of the epoxy foam (near 60 °C) using the tan delta peak. The T_g in cross-linked polymers is a function of polymer chemistry and network organisation. The reduction in T_g of the VGCNF/epoxy foams is possibly due to the VGCNF disruption of the cross-linking network of the matrix to decrease the effectivity of the cross-link



Fig. 6. Storage modulus and tan delta of the epoxy and 1.0 wt% VGCNF/epoxy foams from DMA testing.



Fig. 7. Four-step thermo-mechanical cycle: (1) compression to a maximum strain of 80% at 65 °C, (2) cooling to 25 °C with ε_m kept constant, (3) holding for 10 min at 25 °C under no load, and (4) heating to 65 °C under no load. The red and green lines are the stress-strain-temperature curves the epoxy and VGCNF/epoxy foams, respectively, obtained in the thermo-mechanical cycle test under the maximum strain of 80%.

density [18,22]. Consequently, epoxy foams with a low glass transition temperature and a low free shape recovery temperature were obtained.

3.6. Thermo-mechanical cycle test

The stress-strain-temperature curves of the epoxy (the red¹ line) and VGCNF/epoxy (the green line) foams obtained in the ther-

 $^{^{1}\,}$ For interpretation of colour in Fig. 7, the reader is referred to the web version of this article.



Fig. 8. Relationship of the shape recovery and fixity ratios to the cycle number of the VGCNF/epoxy and pure epoxy foams.

mo-mechanical cycle test using the maximum strain ($\varepsilon_m = 80\%$) are shown in Fig. 7. The four steps associated with the shape fixity and recovery is highlighted. Shape fixity and recovery ratios are two important parameters for determing, and evaluating SMP characteristics, as defined by (1). The shape recovery and fixity ratios are determined in terms of the strain [15,23], where *N* is the number of thermo-mechanical cycles (*N* = 1 in Fig. 7), *R*_f is the shape fixity ratio, *R*_r is the shape recovery ratio, ε_m is the pre-deformation strain (strain at the end of step 2), ε_u is the temporary strain fixed (strain at the end of step 3) and ε_p is the permanent strain (strain at the end of step 4).

The relationship of the shape fixity and recovery ratios to the cycle number is shown in Fig. 8. The shape fixity ratios are clearly very high (approximately 94% R_f for the two foams), suggesting a good shape fixity of the smart foams. In the first cycle, the shape recovery ratios are approximately 95% for the epoxy foam and 98% for the epoxy foam reinforced with 1.0 wt% VGCNFs. This result suggests that the incorporation of VGCNFs enhances the shape recovery ratio of the epoxy foam. However, both foams have a shape recovery ratio of more than 98% after the second cycle. The ratio tends to be a constant 99% with increased cycle numbers. This phenomenon is called "training" effect [23].

Fig. 9 shows that approximately 10 s is required for shape recovery at 65 °C, which is relatively quick considering a size of 18 mm × 13 mm × 13 mm and a bulk density of 0.29 g/cm³. The shape memory effect allows the foam to recover from a large strain after being packed in a temporary shape. This effect is driven by the entropic behaviour in the polymer chains between the cross-links of the epoxy. Below T_{g} , the polymer chains between the



Fig. 10. Relationship between the electrical conductivity and cycle numbers of the VGCNF/epoxy foam at four strains (60%, 70%, 80% and 90%). The inset shows the electrical conductivity of the epoxy foam (green triangle) and VGCNF/epoxy foam (red square). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

network points cannot undergo any conformational changes and are locked into shape unless a suitably large mechanical force is applied. The chains can undergo rotational conformation changes at relatively lower stresses when heated to T_g . As the polymer deforms above T_g , the polymer chains begin to align, increasing the stored energy in the material as the entropy of the chains decreases. Upon cooling in the deformed shape, the polymer chains can no longer freely rotate. The polymer chains then recovered this stored energy by returning to the initial high entropy configuration when the material is heated above T_g without constraint, returning to the initial shape [18].

Therefore, the very high shape fixity and recovery ratios suggest the good SM functionality of the VGCNF/epoxy foam prepared via latex technology. The stable recovery of VGCNF/epoxy foams is achieved after several training cycles.

3.7. Electrical conductivity after four thermo-mechanical cycles

Fig. 10 shows the electrical conductivities of the epoxy foams before and after VGCNF addition, as well as that of the VGCNF/ epoxy foams after four cycles at four different strains. The test results did not show any significant decrease in the electrical conductivity of the VGCNF/epoxy foams after thermo-mechanical cycles at 60%, 70%, and 80% strain. Meanwhile, the electrical conductivity of the foam at 90% strain is markedly reduced. The foam



Fig. 9. Shape recovery behaviour of the VGCNF/epoxy foam at 65 °C.



Fig. 11. SEM images of the epoxy foam and the recovery VGCNF/epoxy foams after four thermo-mechanical cycles: (A) original foam, (B) 80% strain, and (C) 90% strain.

cell wall or cell strut is well protected at 80% strain after four thermo-mechanical cycles, whereas the foam cell wall is severely damaged at a strain level as high as 90% (Fig. 11). The decreased electrical conductivity can be attributed to the breakage of the foam cell wall, leading to the destruction of the conductive network created by the VGCNFs in the epoxy matrix.

4. Conclusions

Epoxy foams composed of VGCNFs and SMP foams were prepared via latex technology. Their mechanical properties and shape recovery behaviours were investigated. Based on a comprehensive test programme, the following conclusions are obtained:

- (1) The glass transition temperature of the epoxy foams decreased with the addition of 1.0 wt% VGCNFs. The strengths of the VGCNF/epoxy foams under the deformation strain of 80% were higher than that of the pure epoxy foam.
- (2) The epoxy foams had good SM functionality and can maintain their high shape recovery and fixity ratio at more than 90% after several thermo-mechanical cycles.
- (3) For the VGCNF/epoxy foam, the percolation threshold for conduction was approximately 0.6 wt% and the electrical conductivity was approximately 10 orders of magnitude larger than that of the epoxy foam. No significant decrease was noted in the electrical conductivity of the VGCNF/epoxy foam during several thermo-mechanical cycles below 80% strain. However, the electrical conductivity rapidly decreased at 90% strain.
- (4) Compared with the conventional method for epoxy based foam preparation, the latex technology has great advantages, such as convenience and environmental friendliness. Moreover, this technology can be applied to both liquid and solid epoxy resins.

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Appendix A

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m}, \text{ and } R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)}$$
 (1)

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