Composites Science and Technology 94 (2014) 23–29

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Self-healing epoxy via epoxy–amine chemistry in dual hollow glass bubbles

He Zhang, Pengfei Wang, Jinglei Yang *

School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore

ARTICLE INFO

Article history:
Received 2 December 2013
Received in revised form 10 January 2014
Accepted 12 January 2014
Available online 21 January 2014

Keywords:
A. Smart materials
A. Self-healing epoxy
B. Fracture toughness
D. Fractography

ABSTRACT

Etched hollow glass bubbles (HGBs) with through-holes at micron level were used as micro-containers for epoxy and amine solution to realize the self-healing functionality in epoxy matrix. The average diameter, the average shell thickness, as well as the cavity inside the shell were investigated. In order to check the mechanical robustness and the rupturability of the HGBs, micro-compression tests of single HGB were conducted to measure their mechanical responses, which reveal the relatively high compressive strength and brittle feature. A new type of self-healing epoxy was developed based on the dual HGB carriers and the self-healing performance was optimized systematically to obtain better healing behavior. It is found the highest healing efficiency of about 62% was achieved at 50 °C for 24 h when 12.5–15.0 wt% healing agent carriers was incorporated at the optimized ratio of 4:1 for epoxy loaded HGBs (HGB-E) to amine loaded HGBs (HGB-A). It is also found that the healing efficiency increased with increased healing duration at 50 °C. In addition, the fracture toughness is improved and the tensile modulus keeps constant while the tensile strength is deteriorated by the incorporation of the carriers.

1. Introduction

As an extensively used engineering polymeric material, epoxy resin has drawn much attraction due to its excellent physical, chemical, as well as thermal properties. The wide range of applications for epoxy includes the functional coatings, the electronic/dielectric components, structural adhesives, and most importantly the composites as the adhesive and protective matrix [1]. However, this thermoset with high cross-link density is very brittle, leading to its high sensitivity to in-born defects or force-induced cracks. Variety approaches have been proposed to improve the fragile feature of the epoxy resin, among which the incorporation of self-healing functionality [2–4] is very promising because of the toughening effect by the added healing agent carriers as micro-fillers [5] and the re-bonding of the induced micro-cracks timely upon their formation. Self healing in epoxy can be realized by various means in different scales, such as by layup of hollow tubes [6–12], fabrication of micro-vascular networks [13], microencapsulation [14–21], thermal additives [22], as well as molecular design by Diles-Alder reaction [23]. Attributed to the ease of manufacture and material integration, the embedment of microcapsules containing healants is the most popular approach among all the methods.

Nowadays, the homogeneous healing of epoxy with epoxy-hardener chemistry has been attracting more and more attention. Because epoxy monomers can be easily incorporated to the epoxy matrix by different methods, the embedment of hardeners into epoxy matrix is the key point for the homogeneous healing. Previously some secondary hardeners for epoxy, like latent curing agent [24], polymercaptan [16], and cationic catalyst [17,18], have been adopted to realize the homogeneous healing in epoxy. Recently, the widely used amine and amine derivative hardeners were also encapsulated by various methods, including reverse emulsion method [25], solvent evaporation method [26] and loading by synthesized hollow poly(ureaformaldehyde) (PUF) microcapsules [27,28]. However, the polymeric shell would be corroded by the highly corrosive amine during their service life and would be downgraded by the thermal treatment during manufacturing of the material and their application.

As epoxy is the most widely employed adhesive matrix in composites, it is also very exciting to incorporate the self-healing functionality into composite materials [6,8,12,29–34]. Successful cases with good healing performance were reported via various self-healing approaches similar as in the pure epoxy matrix. Considering the much harsher processing conditions for composite materials, such as repeatedly brushing the adhesive, pressing to remove the excess amount of the adhesive, relatively high post heat-treatment temperature up to hundreds centi-degree, the carriers for the healing agents should be strong enough to survive from the manufacturing of the composites. Keller and Sottos [35] tested the elastic stiffness and the strength of the PUF shell, revealing that the microcapsules with smaller diameter have a higher normalized failure strength while failing at lower loads. Yang et al. [36] also tested the mechanical properties of the synthesized

* Corresponding author. Tel.: +65 6790 6906.
E-mail address: MJLYang@ntu.edu.sg (J. Yang).

0266-3538/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compscitech.2014.01.009

polyurethane (PU) microcapsule containing diisocyanate, finding that the PU shell is relatively brittle compared with the flexible feature possessed by the PUF shell. Although the higher strength of the carrier does not always mean better healing behavior considering the rupturability of the carrier at the crack plane upon the fracture event, the relatively higher strength of the carrier enables the higher survivability of the carriers. Combining with the corrosive feature of some healing agents and thermally degradability of the shell, to explore healing carriers with relatively higher strength, chemical inertness, as well as thermally stability, is one direction to advance the self-healing materials.

HGBs can be very attractive alternative carriers for healing agents considering their good mechanical properties, thermal stability up to thousand centi-degree, and excellent inertness to most chemicals. In our previous investigations, we have reported the etching of HGBs with diluted hydrofluoric acid (HF) using a specially designed reaction system and their applications as microcontainers for self-healing agents [37–39]. When the etched HGBs loaded with amine solution and the microcapsules containing epoxy solution were mixed into epoxy matrix, satisfactory healing performance was achieved in this system. However, the system is not good to be used in composites materials due to the difficulty of synthesizing small epoxy microcapsules with good flowability and the relatively low mechanical strength of the PUF shell. In order to avoid the usage of epoxy microcapsules, we reported the fabrication of self-healing epoxy via both epoxy monomer and amine solution carried by etched HGBs.

2. Experiment

2.1. Materials

Epoxy and related hardener, Epolam 5015 (ρ_{5015} = 1.150 g/cm^3) and hardener 5015, were purchased from Axson. Neopentyl glycol diglycidyl ether (NGDGE, ρ_{NGDGE} = 1.04 g/cm^3) as the reactive diluents for epoxy, diethylenetriamine (DETA, ρ_{DETA} = 0.951 g/cm^3), 2,4,6-tris(dimethylaminomethyl)phenol (DMP 30, ρ_{DMP} = 0.969 g/cm^3) as the epoxy curing accelerator, acid yellow 73 as the color indicator, were ordered from Sigma Aldrich. HGBs were bought from 3 M. All the chemicals were used as received from the suppliers.

2.2. Etching of HGBs

The adopted HGBs with through-holes were etched using a specially designed reaction system, as reported in our previous report [37]. Sieved HGBs with diameter from 63 to 90 μm were first water-deposited to remove the debris. 2 g HGBs, enough deionized (DI) water, were charged into the container while 160 ml etching agent, 1% diluted HF solution, was charged into the feeder. Under stirring at 45 rpm, the HF solution was added into the mixture in the container at feeding rate of about 35–40 drops/min. After about 12 h, the process was ceased, and the etched HGBs depositing at the bottom zone were collected. In order to completely remove the free fluorochemicals in the collection, the HGBs were rinsed with DI water for 3–4 times. The HGBs were dried at room temperature (RT~20 °C) for 24 h and water-deposited again using a separation funnel to remove the debris. The process was repeated for 3–4 times for better quality. Finally, the floating HGBs in the separation funnel were collected and dried at RT for 24 h as the target product.

2.3. Mechanical characterization of the collected HGBs

The compressive properties of the etched HGBs with through-holes were conducted using single microsphere compression apparatus as reported by Keller and Sottos [35] and Yang et al. [36]. The schematic configuration can be found in the inset in Fig. 2a. The employed loading rate for the stepper actuator (Physik Insturmente M-230S) was 2 μm/s and was controlled by a computer. The load was recorded by a 0.5 N load cell (FUTEK). Images were taken prior the compression tests to measure the diameter of the HGBs.

Before tests, the HGBs were added into acetone solution in a 20 ml vial. One small drop of the mixture with several HGBs was transferred to the bottom of the compression rod. After the evaporation of acetone, extra HGBs were removed carefully to leave only one bubble at the end of the rod.

2.4. Loading of the HGBs with healants using the vacuum-assisted method

The vacuum-assisted device and related method for the loading with amine solution was illustrated in our previous report [37]. Briefly, the HGBs were charged into a two-neck flask with one neck connected to a vacuum pump and another neck equipped with a separation funnel for the addition of amine solution. After 30 min's evacuation, the outlet was blocked and the amine solution, DETA with 10 wt% DMP 30, was fed in through the separation funnel. The system was hold for about 30 min for the full infiltration of amine solution into the cavity of the HGBs. And finally the HGBs with amine solution inside were separated by absorbing away the residual amine solution by tissues, and collected as the target product for further usage.

As the epoxy solution to be loaded, Epolam 5015 with 30 wt% NGDGE, is a little viscous, warm-up of the system and the solution to about 80 °C was executed to reduce the viscosity. Vacuum pump was employed to assist the removal of the residual epoxy solution outside.

The equivalent hydrogen weight (EHW), defined as the weight in grams that contains 1 mol equivalent of reactive hydrogen atom, is 22.89, based on the composition of the amine solution and the theoretical functionality of DETA (n = 5). The density of the loaded amine solution is 0.953 g/cm^3 based on the ratio of the gradients. According to the composition of Epolam 5015 [40] and ratio of each gradients, we can estimate that the equivalent epoxide weight (EEW), defined as the weight in grams that contains 1 mol equivalent of epoxide, of the loaded mixer is approximately 133. And the density of the epoxy solution is 1.117 g/cm^3.

2.5. Fabrication and assessment of the self-healing epoxy TDCB specimen

The self-healing behaviour of the epoxy resin incorporated with healing agent carriers could be characterized by the mode I fracture toughness using tapered double-cantilever beam (TDCB) specimen with localized short groove, as stated by Brown et al. [41]. Epolam 5015, and the related hardener 5015, was mixed for about 5 min at the ratio recommended by the supplier, and further degassed for about 15 min to eliminate the trapped air-bubbles. Later, the epoxy loaded HGBs (HGB-E) and amine loaded HGBs (HGB-A) at different ratios and concentrations were dispersed into the mixture uniformly. The mixture was filled into the short groove of the TDCB specimens, cured at RT for 24 h, and further post-cured at 35 °C for another 24 h. In order to investigate the influence of healing time at 50 °C on the healing behaviour, one set of specimen was healed at 50 °C for certain duration.

The self-healing tests were carried out using an Instron testing machine (Instron Mini High Precision Tester). Before the fracture toughness testing, a pre-crack was introduced by a sharp razor. Loading speed of 1 mm/min was adopted for the overhead. After the complete fracture of the specimens along the middle plane at the short groove, the specimens were healed under various conditions at 50 °C for different durations. Healing tests were performed