Self-healing Epoxy with Epoxy-amine Dual-capsule Healing System

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Keywords: Self-healing epoxy, Smart materials, Fracture and fatigue, Healing efficiency.

Abstract. A new type of epoxy composite with self-healing functionality was successfully developed in this work. Self-healing is achieved via embedded microcapsules containing diglycidyl 1,2-cyclohexanedicarboxylate(DGCHD)and microcapsules containing modified aliphatic amine(HB-1618) hardener. This paper also investigated the preparation and properties of curing agent microcapsule which was prepared by the solvent evaporation method. Recovery of impact strength is assessed through izod notched impact testing for impact specimens. It was found that the content of both microcapsules largely influenced the healing efficiency at a certain range. As a result, the optimal filling contents of epoxy-containing microcapsules and hardener-containing microcapsules embedded in the epoxy matrix are 6 wt. % and 9 wt. %, offering a ~65.6% healing efficiency. Scanning electron microscope (SEM) photos of fracture surface before and after healing process proved that the healing process was successfully realized.

Introduction

As a widely used thermoset resin, epoxy resin has attracted great attention because of its outstanding physical, chemical as well as thermal characters[1]. However, this thermoset resin with high crosslinking density is very sensitive to cracks from external force as its brittleness. To address this problem, the materials with ability of self-repairing cracks were proposed[2]. So far, imparting self-healing function to epoxy can be realized through two strategies: intrinsic self-healing and extrinsic self-healing[3]. The former enables crack healing by themselves without additional healing agent. With the latter approach, healing agent is pre-embedded in the matrix by means of fragile pipelines or microencapsulation[4]. For the moment, the embedment of microcapsules containing healing agent seems to be a more promising prospect among all the methods because of the ease of manufacture and material integration. Nowadays, some curing agents for epoxy, like modified amine[5-6], polythiol[7-8], and polyetheramine[9] have been encapsulated and adopted to achieve the homogeneous healing in epoxy. Compared with epoxy itself, the microencapsulation of suitable hardener for curing epoxy is more difficult because the traditional amine hardener is highly active at room temperature. Based on these considerations, in this work, self-healing epoxy composites containing epoxy- and amine-loaded microcapsules were prepared. Crack healing behavior of the composites was discussed in terms of microcapsules content and optimal weight ratio of two types of capsules. Considering that modified aliphatic amine (HB-1618) is very active and some polymers are not suitable for its encapsulation, the solvent evaporation method was adopted to form polymer shells around the reactive amine in this paper.

Experimental

Raw Materials

Microcapsules containing DGCHD were prepared using the method reported by Wang et al.[10]. An average microcapsule diameter of 60 μm and core content of 89.1 wt % were obtained at 11000 rpm emulsifying rate. Modified aliphatic amine (HB-1618) and polyetherimide (PEI) were used as core substance and shell material of the hardener microcapsule, respectively. Diglycidyl ether of bisphenol A (E-51; epoxy equivalent weight, 0.51) was employed as the matrix polymer of the self-healing epoxy composites and the curing agent triethylenetetramine (TETA) worked for the matrix.

Preparation of Microcapsules Containing HB-1618

Samples of 2 g PEI and 3 g HB-1618 were mixed with 55 ml dichloromethane (DCM). Then the mixture was added to 90 ml of gelatin solution (1.0 wt %) under high speed agitation at room temperature to get an O/W pre-emulsion. The resulting mixture was then poured to a 275 ml gelatin solution (1.0 wt %) with continuous stirring. DCM was allowed to evaporate completely in an open vessel for 7 h at 35^{o}C. The prepared microcapsules were collected by filtration, rinsed with deionized water and finally dried.

Preparation of Self-healing Epoxy Samples

The resin mixture was produced through mixing 100 parts E-51epoxide, 15 parts 1,4-butanediol diglycidyl ether with 11.4 parts TETA. Then, the different concentrations and weight ratios of the capsules containing DGCHD and its hardener HB-1618 were added to the aforesaid E-51/TET-A mixture. The resin mixture was degassed, poured into a closed polytetrafluoroethylene mold, and cured for 48 h at room temperature, followed by 2h at 80 ℃.

Characterization

Surface morphology of microcapsules and fractured surface of self-healing epoxy were observed using SEM (FESEM-Hitachi SU8000, Japan), while the microcapsules size distribution was measured with a Master Sizer 2000 size analyzer. Thermo gravimetric analysis (TGA) was performed on a Netzsch TG-209 in N_2 at a heating rate of 10 ℃ min^{-1}. To evaluate self-healing ability of the materials, the protocol proposed by Jones et al.[11] was used as follows. The healing efficiency is defined as the ratio of impact strength of healed and virgin materials. Izod notched impact tests were conducted at 25 ℃ according to ASTM D 256-03 using a ZBC1100-A impact tester produced by MTS Systems Corp., China. After testing, the specimens that had been broken into two pieces were kept in alignment and intimate contact for healing at 100 ℃ for 1 h. Finally, the healed specimens were tested again following the above procedure. Five specimens were tested to yield mean value for each batch.

Results and Discussion

Properties of HB-1618 Microcapsules

Figure1 shows the size distribution of hardener-loaded microcapsules as well as the corresponding SEM image. As shown in Figure 1, the microcapsules have relatively uniform sizes and it can be estimated that the average particle size of the microcapsule is 25.5 μm. Besides, the microcapsules present a regular spherical configuration and the outer surface of the microcapsules is smooth. Figure 2 shows the TGA curves of microcapsules, HB-1618 and PEI shell. The thermal decomposition of the PEI shell shows only one step weight loss in the range of 500-600^{o}C. As for the curing agent HB-1618, two stage weight losses have been observed. In addition, microcapsules exhibit a three-stage of weight loss from 140 to 600^{o}C. The two previous weight loss starts at 140 ^{o}C produced by the weight loss of HB-1618 from the broken PEI microcapsules. The decomposition temperature of the core materials has been shifted higher owing to the protection of the PEI shell. This indicated that HB-1618 was entrapped successfully in PEI. Content of HB-1618 in the microcapsules is noted to be about 40 wt %, which is estimated from the weight loss of microcapsules between 140 and 450^{o}C.

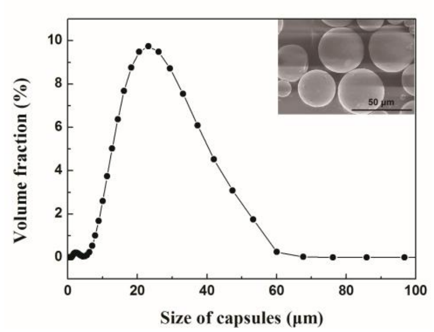

Fig. 1 Size distribution and SEM micrograph of capsules containing HB-1618.

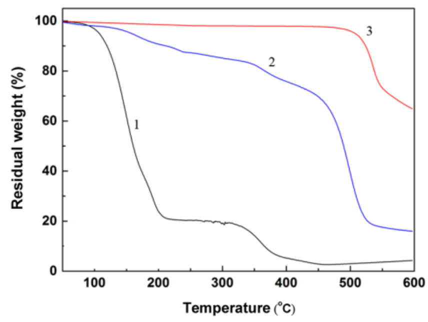

Fig. 2 Thermogravimetric analysis of the related materials and microcapsules.1:HB-1618; 2: Microcapsules containing HB-1618; 3: PEI shell.

Effect of Microcapsules on Self-healing Performance

The influence of the total concentration of the two capsules on healing efficiency is shown in Figure 3 in terms of fracture strength recovery. As exhibited in Figure 3, at a constant ratio 1.5:1 for hardener capsules to DGCHD-filled capsules, the healing effciency increases with microcapsules' content and the maximum value (142.3%) is obtained for the 20 wt % of microcapsule filled epoxy. However, impact strength of the specimens gradually decreases with increased the concentration of microcapsules. Especially, the impact property of the virgin self-healing specimen decreases sharply when the total concentration of the dual capsules exceeded 15 wt %. As a result, the optimal total concentration of microcapsules is 15 wt%.

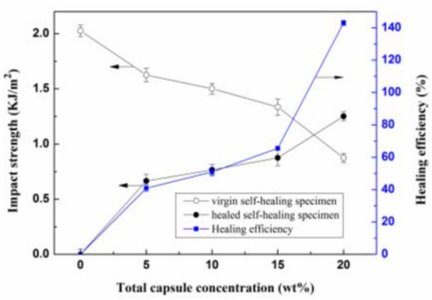

Fig.3 Influence of microcapsules' content on impact strength and healing efficiency. Weight ratio of hardener-/DGCHD-filled capsules in all the self-healing specimens is 1.5:1.

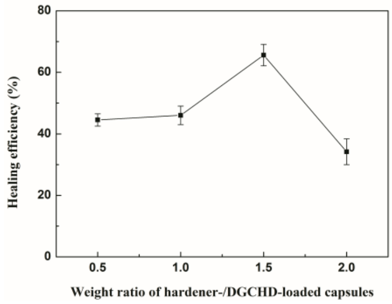

Fig. 4 Effect of weight ratio of embedded hardener- to epoxy-loaded capsules on healing efficiency. Microcapsule concentration was 15 wt % in all samples.

Further analysis of the influence of mass ratio of hardener-/epoxy-loaded capsules with the total capsules concentration of 15 wt% (Figure 4) suggested that maximum healing efficiency of about 67% was obtained when the ratio of hardener- /epoxy-loaded capsules was held at 1.5:1.

SEM of Healed Fracture Surface

Fracture surfaces were photographed using SEM to determine the effectiveness of the microcapsule in providing adhesive membrane. From Figure 5a, it can be seen that after failure of the first impact test the microcapsules must be cleaved and the healing agent had flowed out, leaving the concaves. Having been healed and after the second impact test, the cured healing membrane is apparent on the fracture plane (Figure 5b). These facts show that healing process is successfully reached.

Fig. 5. SEM images of fractured surface of self-healing epoxy composite with 6.0 wt % DGCHD-filled capsules and 9.0 wt % hardener-loaded capsules: (a) virgin specimen and (b) healed specimen.

Conclusions

In this work, a self-healing epoxy composite with microencapsulated healant had been developed. Two types of microcapsules were utilized, one containing highly flowable epoxy prepolymer. The second microcapsule containing modified aliphatic amine (HB-1618) was fabricated using solvent evaporation method and the core content of about 40 wt % was achieved. Impact testing demonstrates the capsules content and the weight ratio of hardener- to epoxy-loaded capsules greatly affect the healing efficiency, the optimal weight ratio of hardener-/epoxy-loaded capsules is 1.5:1 and the capsules concentration is 15 wt %. In general, the present work provides a new system for producing self-healing materials using epoxy microcapsules.

Acknowledgments

The authors are grateful for the support of the Scientific Research Fund of Hubei Provincial Education Department (no.B2013162) and the Opening Project of Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jianghan University (no. JDGD-201604).

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