Investigating the Bending Behavior of Self-Healable Epoxy-Glass Fibers Composites

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Abstract:

Utilizing self-healable systems in the composite structures as a new kind of smart materials is a new way to recover the mechanical properties such as bending properties in these structures. Therefore, this work aims to investigate the bending properties of epoxy- glass fibers composites containing microcapsules (as healing agent container). It is worth noting that the healing agent was the same epoxy resin which was used in the matrix. To do so, in the first step, the microcapsules containing epoxy as healing agent were synthesized by urea formaldehyde shell trough in situ polymerization. It should be noted that, the microcapsulation process was the one stage method. Then, the 7 wt.% microcapsules and 2 wt.% $NiCl_2$.(imidazole)$_4$ were dispersed into the epoxy matrix. In the following, the epoxy- glass fibers composite were fabricated by the hand lay-up technique by placing four layers of glass fibers. To study the healing behavior in the bending test, the samples were initially damaged by the quasi static penetration method. In order to create the matrix cracks, delamination between layers and fiber fractures damages, three damage forces (400, 500 and 600 N) were selected. The created damages were caused to rupture the microcapsules and diffuse the healing agent in the damaged area. The healing agent could fill the microcracks a few minutes after the creating the damages. To active the catalyst for healing, the damaged composites were set into the oven in the temperature of 130 ˚C for the period time of 1 h. After that, the bending tests were carried out according to ASTM D790 standard. Also, the microstructure investigations were done by optical microscope (OM) and field emission scanning electron microscope (FESEM). The obtained flexural strength for undamaged sample was 308 MPa. Also, the flexural strength of damaged composites in the damage forces of 400, 500 and 600 N were 199, 171.25 and 164.6 MPa, respectively. The healed sample with damage force of 600 N had the flexural strength of 204.5 MPa which was minimum flexural strength, as comparison with other samples, due to glass fibers breakage in the composite. Also, the healed samples with damage forces of 400 and 500 N had 285.8 and 251.6 MPa flexural strength after the healing process. The obtained healing efficiency for the healed samples with the damage force of 400, 500 and 600 N were 79, 58.4 and 27.6 %, respectively. As the most important finding of this work, it was realized that the microcapsules containing epoxy healing agent and $NiCl_2$.(imidazole)$_4$ catalyst could properly heal the matrix cracks and delamination phenomenon, but had a poor mechanical recovery in the sample with the fibers breakage phenomenon.

Keyword: *Composites; Glass fibers; Self-healing; Microcapsules; Bending Properties.*

1 Introduction

The development of cracks in composites and polymer materials is a major problem during their service. The growth of micro-cracks and incorporation of them together can lead to catastrophic failure. Using the self-healing system into these structures is one of the important ways which has been developed by researchers in the last decade [1, 2]. The healing system based on microcapsules as container of healing agent was introduced as extrinsic system by Brown et al. [3]. In this system, the healing agent is capsulated by polymeric shell such as urea- formaldehyde, melamine formaldehyde and poly methyl methacrylate. After that, these microcapsules are dispersed into the polymeric matrixes like epoxy resin [4]. The healing proceeding includes three steps which are reaching cracks to the microcapsules and failure of them, diffusing the liquid inside microcapsules to the cracks and healing the cracks by the polymerization reactions [5].

To start the polymerization reaction for healing system, the second agent should be used. Therefore, in this system, the proper catalyst of healing agent is used. The first introduced catalysts were first and second generations of Grubb's catalyst [6]. Another used catalyst for healing system was WCl_6 which was introduced by Haiyan et al. [7]. In the study of Yin et al. [8], the $CuBr_2$.(2-methyl imidazole)$_4$ was used as a new generation of catalyst for the polymerization of epoxy based healing system. The aim of this research work is to investigate the bending properties of epoxy- glass fibers self-healable composites. It is worth noting that the epoxy healing agent were capsulated by the urea formaldehyde shell. The synthesized microcapsules with the imidazole based catalyst were dispersed into the epoxy matrix.

2 Materials and methods

In order to fabricated the glass fibers- epoxy self-healable composites, the urea (Pardis Petrochemical Company, Iran), sodium dodecyl sulfate, ammonium chloride and formaldehyde solution (Dr. Mojallali Industrial Chemical Complex Company, Iran), 1-octanol, resorcinol and imidazole based catalyst (Merck, Germany), epoxy 828 resin and TETA hardener (Kumho P&B Chemical, Korea), as well as plain weave glass fabric with surface density of 400 g. cm^{-2} (Lintex, China) were used.

To synthesize the microcapsules containing epoxy healing agent, the Brown's method was used [3]. To do so, 0.2 g sodium dodecyl sulfate, 2.5 g urea, 0.25 g ammonium chloride and 0.25 g resorcinol were firstly added to 150 ml deionized water. Then the solution was mixed by 3-blade mechanical mixture with the rate of 600 rpm. After 15 min, the pH of solution was set on 3.5 by hydrochloric acid. In the following, 2 droplet 1-octanol was added to remove the extra bobbles. In the next step, 20 ml diluted epoxy resin by ethyl acetate was slightly added to the solution. After 15 min, 6.4 g formaldehyde solution was added. The temperature of solution was raised to 55 ˚C and maintained in this temperature for 4 h. In the final step, the formed microcapsules were separated by filtration and air dried for 24 h.

The 7 wt.% synthesized microcapsules and 2 wt.% $NiCl_2$.(Imidazole)$_4$ catalyst were firstly dispersed into the epoxy matrix. After that, the TETA hardener were added and mixed. In the following, the glass fibers- epoxy self-healable composite was fabricated with 4 plies glass fabrics by hand lay-up method. To reach the maximum post curing, based on the suppler recommendation, the fabricated composite was set in the ambient temperature for 1 week.

To investigate the healing ability and bending properties of the fabricated composites, the composites were cut with dimensions of 100×15 mm^2 as per ASTM D790 standard. After that, three kind of samples were introduced which were virgin, damaged and healed samples. In order to creation the initial damages in the composite structures, the quasi-static penetration method with the damage force of 400, 500 and 600 N as per ASTM D6264 standard was used. It should be noted that these forces were selected to cause the matric cracks, delamination between layers and fibers breakages in the composite structures. After that, the damaged samples were set into oven in the temperature of 130 ˚C for period time of 1 h, to heal the created damages. In the final step, the bending tests of the virgin, damaged and healed samples were done with the cross head speed of 3.5 $mm.min^{-1}$. The healing efficiency of composite structure was calculated from [1] equation (1):

$$\eta = \frac{\sigma_{healed} - \sigma_{damage}}{\sigma_{virgin} - \sigma_{damage}} \quad (1)$$

Where, σ_{healed}, σ_{damage} and σ_{virgin} are flexural strength of healed, damaged and without damaged samples, respectively. To characterize the synthesized microcapsules and the healing effect in the microstructure of composite, the field emission scanning electron microscope (FESEM), Mira3 Tescan- Czech, and optical microscope (OM), Meiji techno- Japan, were used.

3 Results and discussion

3.1 Microcapsules

Figure 1 shows the synthesized microcapsules containing epoxy healing agent which the average diameter of them is 250±50 µm. Also the thickness of urea formaldehyde is 320 ± 20 nm. One of the important factors to heal the composite structure is the core content of synthesized microcapsules which is calculated by extraction method [1]. Therefore, the obtained core content of these microcapsules is 72.5 %.

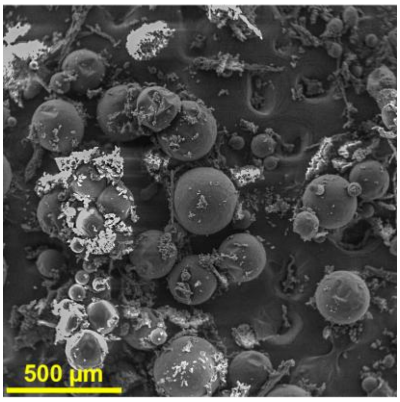

Figure 1. The FESEM image of synthesized microcapsules containing epoxy healing agent.

3.2 Bending properties

The obtained results from bending test have been summarized in the table 1. From table 1, it can be understood that the samples with the damage forces of 400, 500 and 600 N had 199, 171.25 and 164.6 MPa remained flexural strength, respectively, which approximately reduced 35, 44 and 46.5 %, as compared with the virgin sample. After the healing process, the flexural strength of them reached to 285.6, 251.6 and 204.5 MPa, respectively. Based on the table 1 and equation (1) the healing efficiency of the samples was calculated which can be seen in Figure 2.

Table 1. The obtained results from bending test

damage force (N)	σ_{virgin} (MPa)	σ_{damage} (MPa)	σ_{healed} (MPa)
400	308.00	199.00	285.80
500	308.00	171.25	251.60
600	308.00	164.60	204.50

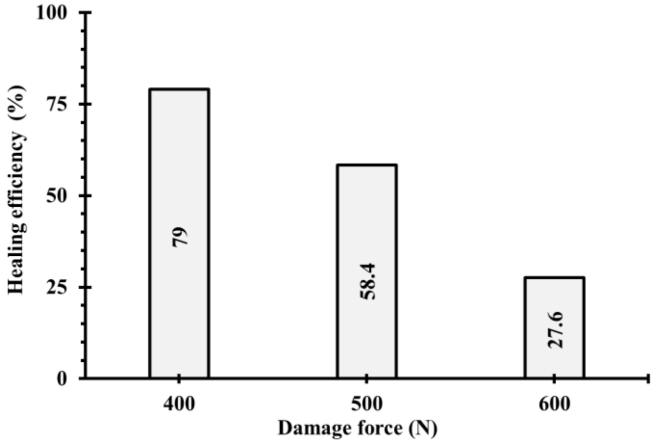

Figure 2. The healing efficiency in the different damage forces.

The obtained healing efficiency for the healed samples with the damage force of 400, 500 and 600 N were 79, 58.4 and 27.6, respectively. Based on the these healing efficiency, it can be said that the microcapsules containing epoxy healing agent and $NiCl_2$.(imidazole)$_4$ catalyst could properly heal the matrix cracks and delamination phenomenon, but had a poor mechanical recovery in the sample with the fibers breakage phenomenon. Figure 3 shows the interaction between microcapsules and cracks under damage forces. According to this figure it can be mentioned that the crack can be ruptured the microcapsules or crossed from interface between microcapsule and matrix. These observed phenomena was confirmed by other literatures [8-10]. The interesting observed phenomenon in this figure was the buckling the microcapsule under the damage forces.

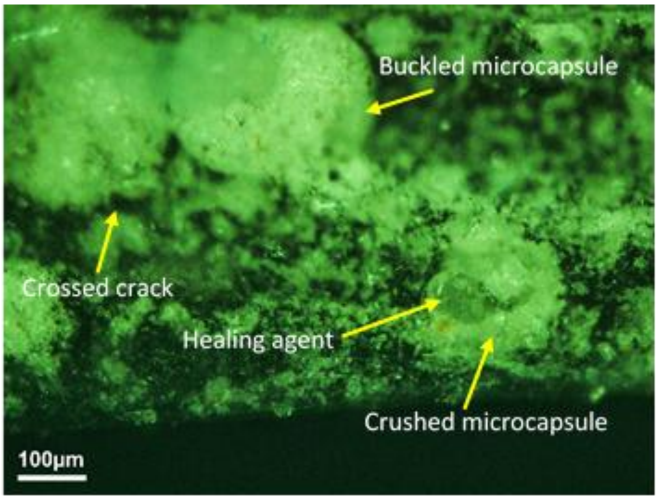

Figure 3. The interaction between microcapsules and cracks.

Figures 4a and 4b show the samples under the damage forces of 400 and 500 N, respectively. In the figure 4a, it can be seen that the healing agent have diffused to the damage area, after the rupturing the microcapsules and have completely filled ones, whereas in figure 4b, the healing agent cannot fill the damage area, due to creation huge crack in the delamination phenomenon. Similarly other literature, after filling the damage area, the healing agent reacted with catalyst and healed the cracks [8].

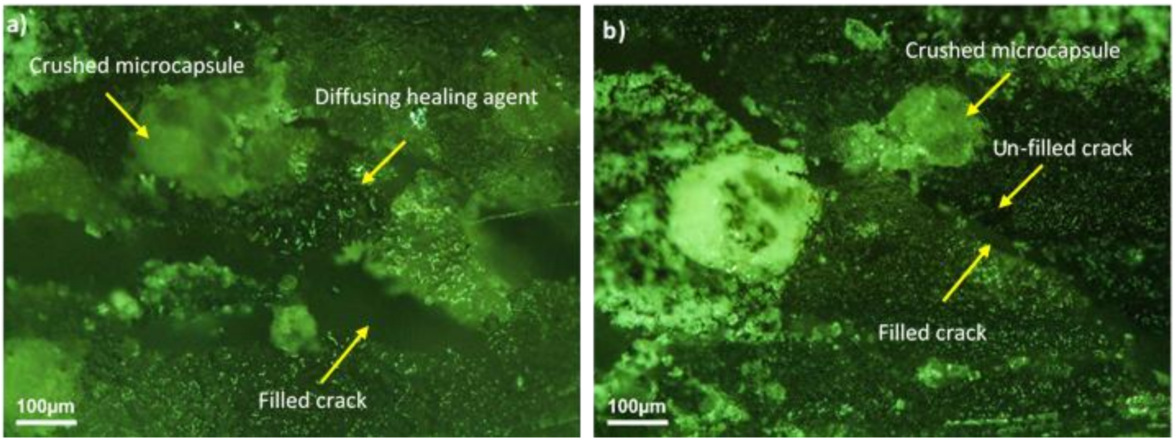

Figure 4. The healing cracks at different damage forces: a) 400 N, b) 500 N.

4 Conclusion

In this work the bending properties and healing ability of epoxy-glass fibers self-healable composite containing microcapsules was investigated. The results of this study can be summarized here:

1. The remained flexural strength of damaged composites in the damage forces of 400, 500 and 600 N were 199, 171.25 and 164.6 MPa, respectively.
2. The healed sample with damage force of 600 N had the flexural strength of 204.5 MPa which was minimum flexural strength.
3. The healed samples with damage forces of 400 and 500 N had 285.8 and 251.6 MPa flexural strength.
4. The healing efficiency for the healed samples with the damage force of 400, 500 and 600 N were 79, 58.4 and 27.6 %, respectively.
5. The crossing, crushing and buckling crack phenomena were observed by optical microscope.

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