EFFECT OF HEALING AGENT-LOADED MICROCAPSULES ON THE MECHANICAL PROPERTIES OF SELF-HEALING EPOXY COMPOSITES

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Abstract
Microcapsules containing a two-component healing agent system suitable for preparing self-healing composites were prepared via oil-in-water emulsion polymerization method with either pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) or epoxy as core material and melamine-formaldehyde (MF) as shell material. The two types of microcapsules were embedded in epoxy resin and carbon fiber reinforced epoxy composite at 5 m% to investigate their effect on the tensile, flexural, fracture and impact properties. Scanning electron microscopy was used to analyze the fracture surfaces. The presence of healing agent-loaded microcapsules softened the matrix, but did not lead to toughening, because the adhesion between the shell wall and the epoxy matrix was unsatisfactory. Microcapsules had a reduced effect on fiber reinforced composites, and even improved adhesion was evidenced by an increase in toughness.

1 Introduction

Microcracking of the polymer matrix can lead to fracture, which is the most dangerous damage form of fiber-reinforced polymer composites. Microcracks can form under various circumstances, e.g. cyclic mechanical load, heat, UV radiation, etc. Conventional methods for repairing microcracks are time-consuming and require manual intervention, or may even be unfeasible. Bio-inspired self-healing polymers however, are able to heal the microcracks autonomously, as damage itself triggers the healing process. One way to add self-healing functionality to a thermosetting polymer matrix is to incorporate special microcapsules in it, that contain liquid monomeric healing agent [1-4]. When a crack appears in the polymer matrix, it ruptures the shell wall of the microcapsules, so the healing agent flows onto the crack surface and cures. Curing can be triggered by a catalyst dispersed in the matrix [1], or by a curing agent embedded in separate microcapsules [5].

Successful self-healing has already been demonstrated by a few research groups [1, 5, 6], and some papers also deal with the effect of the microcapsules on the mechanical properties of the matrix [1, 7, 8]. Regarding the fracture toughness, Brown *et al*. [8] have reported a significant increase that they have attributed to the rubber-like behavior of the liquid-filled microcapsules. On the other hand Yin *et al*. [7] found that the presence of microcapsules deteriorates fracture toughness because stress concentration. Only a few paper deal with the

effect of microcapsules on the mechanical properties of fiber-reinforced composites [9, 10], and only a few properties are tested, so there is a huge need for a detailed investigation.
The aim of this paper is to incorporate healing agent-loaded microcapsules into epoxy matrix and carbon fiber reinforced epoxy composites and to carry out a preliminary study on their effect on the tensile, flexural, impact and - in case of the fiber reinforced composites - the interlaminar shear properties. The effect of the healing agent-loaded microcapsules on the mechanical properties is of crucial importance, as the advantages of self-healing capability cannot result in too much limitation in application. As self-healing composites are most likely to be applied in high-performance applications, carbon fiber was chosen as reinforcement material.

2 Materials and testing methods

2.1 Materials

Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) used as core material that act as curing agent for epoxy, sodium-dodecyl-sulfate (SDS) emulsifier agent, 25 w% hydrochloric acid (HCl) and triethanolamine was purchased from Sigma-Aldrich (Germany). The other core material, the epoxy component MR 3008, with an epoxy equivalent weight of 210-230 g/eq, and a dynamic viscosity of 300-500 mPa·s was purchased from Ipox Chemicals Kft. (Hungary). The wall-forming materials: melamine (M) and 37 w% formaldehyde solution (F) was purchased from Merck KGaA (Germany). Ethylene-maleic anhydride (EMA) used as emulsifier was purchased from Vertellus Specialties Inc. (USA).
As matrix material the same MR3008 modified bisphenol A epoxy component was used, cured with MR3120 aliphatic amine used purchased from Ipox Chemicals Kft. (Hungary). In the composite samples a 200 g/m^2 plain woven carbon fiber fabric (Sygratex KDL 8003) was used, purchased from Novia Kft. (Hungary).

2.2 Preparation of healing agent-loaded microcapsules

To prepare epoxy containing microcapsules, a method published by Alič *et al*. [11] was adopted with some modifications. An emulsion made of 500 ml 0,5 m% SDS aqueous solution and 25 g of MR3008 epoxy component was stirred at 500 rpm for 30 min with a three-blade mechanical stirrer at room temperature (22°C). Meanwhile, 5,8 g melamine and 12,65 g 37 w% formaldehyde solution was heated to 70°C with 5 ml distilled water for 10 min, while pH was set to 9 with triethanolamine. Afterwards, the M-F solution was added the emulsion during continuous stirring, and pH was slowly adjusted to 6 by adding 1 w% HCl solution. When pH 6 was reached, the emulsion was heated to 70°C at a heating speed of 1°C/min. When the target temperature was set, dropwise addition of 1 w% HCl solution was started. During reaction, samples were taken from the beaker to follow the wall forming procedure. After three hours, the reaction was ended. The microcapsules were filtered through a Buchner funnel, rinsed with distilled water and air-dried.
The preparation of PETMP containing microcapsules was somewhat different. A method published by Yuan *et al*. [12] was adopted with some modifications. The emulsion was prepared with 240 ml of 2 w% EMA solution and 80 g of PETMP at 500 rpm, at room temperature (22°C). Meanwhile 12,5 g melamine and 27,1 g 37 w% formaldehyde solution was heated to 70°C with 12 ml distilled water for 10 min, while pH was set to 9 with triethanolamine. After pouring the M-F solution to the emulsion, heating to 65°C was started at 1°/min. When the temperature reached 50-55°C, 300 ml distilled water was added to the reaction mixture to avoid balance the viscosity increase. After two hours of reaction, microcapsules were filtered through a Buchner funnel, rinsed with distilled water and air-dried.

2.3 Specimen preparation

Three types of non-reinforced, and three types of carbon fiber reinforced samples were prepared, the compositions are given in Table 1. The capsules were mixed into the resin mixture of 100 parts of MR3008 epoxy component and 20 parts of MH3120 hardener by hand-mixing, and the resin was poured into a silicon rubber mold. Curing took 24 hours at room temperature followed by 2 hours of post-curing at 80°C. Composite panels were prepared *via* hand lay-up into the same mold to ensure the same thickness. Eight layers of plain woven carbon fiber were used for each type. The panels were cured under pressure under the same conditions as the matrix materials. Samples for the mechanical tests were manufactured with sawing. 110x30x2 mm single edge-notched tensile (SEN-T) specimens were notched with a saw blade and the notch was sharpened with a razor blade to initiate fracture.

	Matrix samples			**Composite samples***		
Composition of the prepared samples	**Reference matrix**	**Matrix with epoxy capsules**	**Matrix with hardener capsules**	**Reference composite**	**Composite with epoxy capsules**	**Composite with hardener capsules**
MR3008 epoxy component [w%]	83.3	79.2	79.2	83.3	79.2	79.2
MH3120 hardener [w%]	16.7	15.8	15.8	16.7	15.8	15.8
Epoxy containing microcapsules [w%]	-	5	-	-	5	-
Hardener containing microcapsules [w%]	-	-	5	-	-	5
Plain woven carbon fiber reinforcement [w%]	-	-	-	8 layers	8 layers	8 layers

* values are given in percentage of the matrix content

Table 1. Composition of the samples

2.4 Testing and characterization methods

Microcapsules and fracture surfaces were characterized by an Olympus BX 51M type optical microscope and a JEOL JSM 6380LA type scanning electron microscope (SEM). Core content of the microcapsules was determined by crushing the microcapsules in a mortar, and extracting the core with acetone. Core content can be calculated from the mass reduction. Tensile, flexural, impact and – in case of the composite samples – interlaminar shear properties were determined according to ISO 527-1:1999 [13], ISO 178:2003 [14], ISO 179-2:2000 [15] and ISO 20505:2005 [16]. Fracture toughness was determined by tensile testing of SEN-T specimens using the Equation (1):

$$K_c = \frac{F_{max}}{B \cdot W} \cdot a^{1/2} \cdot f(a/W), \qquad (1)$$

where F_{max} is the peak force, B is the thickness of the specimen, W is width of the specimen, a is the length of the notch, and $f(a/W)$ is a geometric correctional coefficient (2):

$$f(a/W) = 1{,}99 + 0{,}41(a/W) + 18{,}7(a/W)^2 + 38{,}48(a/W)^3 + 53{,}85(a/W)^4 \qquad (2)$$

Tensile, three-point bending, SEN-T, and interlaminar shear specimens were tested to failure on a Zwick Z050 universal testing machine, whereas Charpy impact test were conducted on a Ceast Resil Impactor Junior type instrumented impact machine. Each test was carried out on a set of five specimens.

3 Results and discussion

Figure 1. shows optical micrographs of the prepared healing agent-loaded microcapsules. Both types of capsules have the same average diameter of 58 μm with a standard deviation of 22 μm. Epoxy capsules have a higher, 85 w% core content, whereas hardener capsules contain 74 w% liquid core material.

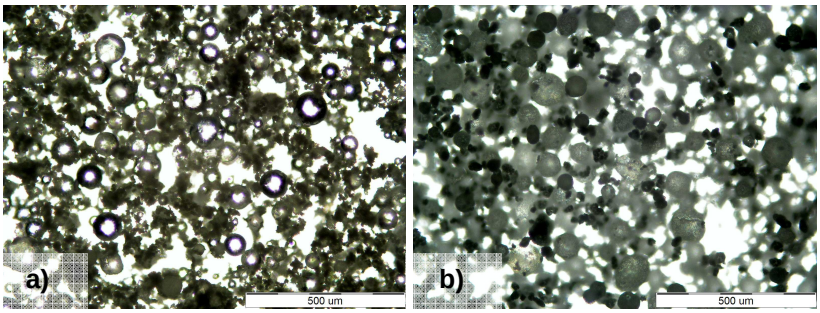

Figure 1. Melamine-formaldehyde microcapsules with PETMP (a) and epoxy (b) as core material

Tensile and flexural testing of the matrix samples revealed that 5 w% loading of either type of the microcapsules causes significant softening of the matrix, evidenced by a 23-38% decrease in tensile strength, 18-19 % and 27-35% decrease in Young's and flexural modulus respectively, and a 157-194% increase in ultimate strain, depending on the capsule type. Detailed results are given in Table 2. An explanation of this softening effect can be that the liquid filled microspheres act similarly to rubber particles. However, the microcapsules failed to provide the expected toughening effect, as both impact strength and fracture toughness decreased by 28-33% and 16-26%, respectively, depending on the capsule type. The possible cause of this phenomenon is the unsatisfactory adhesion between the melamine-formaldehyde capsule wall and the epoxy matrix. SEM pictures of the fracture surfaces revealed that even though many capsules have ruptured during matrix cracking, as expected, several capsules either separated from the matrix, or remained unharmed (Figure 2.). This means that interfacial bonding was not strong enough, so the propagating crack could simply bypass the capsules instead of rupturing it.

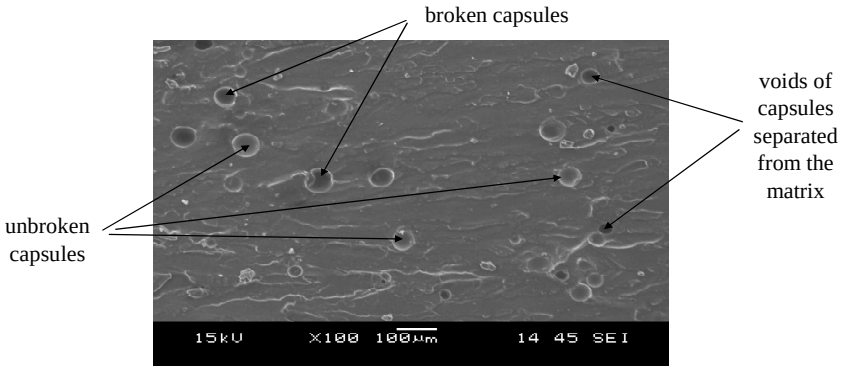

Figure 2. SEM picture of the fracture surface of an epoxy matrix loaded with 5 w% epoxy filled microcapsules

Regarding the applicability, the effect of the microcapsules on the mechanical properties is more important in fiber reinforced composites. As expected, the presence of microcapsules had less effect on the mechanical properties in composites, as they are mainly determined by the fiber reinforcement. Tensile strength, Young's and flexural modulus and ultimate strain of the composites did not change in case of 5 w% epoxy capsule loading in the matrix, whereas incorporation of 5 w% hardener capsules resulted in a 18%, 14%, 13% and 20% decrease,

respectively. Interlaminar shear properties declined by 15-20% with both type of capsules. For detailed results see Table 2.

Mechanical properties of the samples	Matrix samples			Composite samples		
	Reference matrix	Matrix with epoxy capsules	Matrix with hardener capsules	Reference composite	Composite with epoxy capsules	Composite with hardener capsules
Tensile strength [MPa]	31.0±2.69	19.5±0.16	24.3±0.88	465±47.4	473±14.1	379±57.4
Young's modulus [GPa]	1.56±0.06	1.26±0.02	1.28±0.06	9.41±0.76	9.90±0.64	8.11±0.77
Ultimate strain [%]	3.60±0.47	10.6±4.94	9.26±1.71	7.20±0.51	7.16±0.15	6.23±0.64
Flexural strength [MPa]	45.8±0.99	33.8±0.69	29.4±2.20	482±12.1	439±9.73	416±13.2
Flexural modulus [GPa]	1.96±0.03	1.37±0.13	1.04±0.23	22.8±1.73	22.2±1.83	19.8±0.93
Interlaminar shear strength [MPa]	-	-	-	26.3±2.36	20.7±0.54	22.0±0.86
Charpy impact strength [kJ/m^2]	11.4±1.34	7.61±1.22	8.15±0.97	47.1±4.09	60.7±7.49	49.5±5.86
Fracture toughness [MPa*m$^{1/2}$]	2.91±0.27	2.16±0.16	2.45±0.17	28.8±2.16	30.4±2.36	26.25±0.98

Table 2. Results of mechanical testing of epoxy matrix and carbon fiber reinforced composite filled with 5 w% epoxy or hardener capsules

Surprisingly, in the fiber reinforced composite system the epoxy capsules were able to increase toughness, evidenced by a 30% increase in Charpy impact strength and a 5% increase in fracture toughness. The hardener capsules failed to provide the same toughening effect; they even reduced fracture toughness by 9%. A possible explanation of this difference in the effect of epoxy capsules on the mechanical properties in case of matrix and composite samples is that due to the impregnation process during hand lay-up of the composite panels better adhesion can develop between the capsule wall and the matrix. In case of hardener capsule loading, the results lead to the conclusion that the strong mechanical impact during hand lay-up mostly destroyed the capsules, so they act more like stress concentration points instead of toughening. The fact that the hardener capsules decreased the tensile strength and the ultimate strain at the same time supports this hypothesis. Optical micrographs of epoxy and hardener capsule loaded epoxy matrix samples also revealed that epoxy capsules can better withstand processing, as hardener capsules clearly have a more crinkled, damaged shell (Figure 3.).

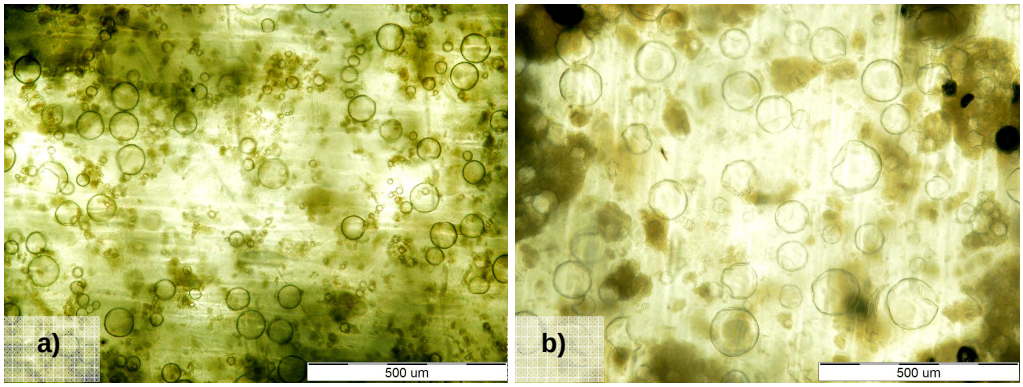

Figure 3. Optical micrographs of epoxy (a) and hardener capsule (b) loaded epoxy matrix samples

4 Conclusions

In this preliminary study the method for preparing epoxy and its curing agent PETMP loaded melamine-formaldehyde microcapsules that are suitable for realizing self-healing epoxy composite was demonstrated. The effect of embedding these microcapsules into epoxy matrix and carbon fiber reinforced epoxy composite on their various mechanical properties, such as tensile and flexural behavior, impact strength, fracture toughness and interlaminar shear

strength was investigated. It was found that 5 w% microcapsules causes significant softening of the epoxy matrix, but fails to provide toughening. SEM pictures revealed that due to poor adhesion, not every microcapsule ruptured during matrix cracking, which can explain the reduced toughness. However, in case of carbon fiber reinforced composites, a different behavior was found. Epoxy capsules did not change the tensile and flexural properties, and managed to increase impact strength and fracture toughness by 30 and 5%, respectively. It was explained by better adhesion due to the impregnation process during hand lay-up. Hardener capsules likely have been crushed during the preparation of the composite panels, as they acted like stress concentration points, evidenced by the reduced strength, ultimate strain, modulus and toughness.
To be able to prepare high-performance self-healing composites, it would be necessary to find a way to make hardener capsules that can better withstand processing, just as epoxy capsules. Also, as better adhesion would lead to better mechanical and self-healing performance, interfacial bonding should be improved, e.g. by applying a coupling agent.

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