Effect of the incorporation of a microencapsulated healing agent in an epoxy-amine fiber reinforced composite material

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Received: 14 December 2016, Revised: 14 February 2017 and Accepted: 07 April 2017

DOI: 10.5185/amlett.2017.1550
www.vbripress.com/aml

Abstract

The objective of this work was to study the effect of incorporating a microencapsulated healing agent in an epoxy matrix and E-glass fiber reinforced composite. Microcapsules were prepared via oil-in-water emulsion polymerization method with dicyclopentadiene as core material and poly(urea-formaldehyde) (PUF) as shell material. The suitable formulation for the epoxy matrix was selected based on the study of the rheological and mechanical properties of various chemical systems. Different amounts of microcapsules were incorporated and the most appropriate processing method (mixing, curing and post-curing cycle) was evaluated. Furthermore, flexural and fracture tests were carried out and the distribution of the capsules as well as the interfacial adhesion with the epoxy matrix were studied. Finally, the processing of fiber reinforced composites, with and without microcapsules, was carried out by compression molding and the mechanical properties of the composites were studied (modulus and maximum flexural strain) from testing three-point bending. The resulting samples with 32 wt. % of fibers and matrices with no microcapsules were compared. Compression molding technique did not affect the integrity of the microcapsules inside the composites. Copyright © 2017 VBRI Press.

Keywords: Epoxy, microcapsules, processing, mechanical properties, fiber composite.

Introduction

Composite materials are man-made combinations of several different materials that produce a new material with unique properties, such as improved stiffness, low density and tailored thermal or electrical conductivity. A large part of these materials combines stiffness and light weight, in particular those designed for transport or aerospace applications.

Epoxy resins are widely used as matrices for the manufacturing of composite materials. Epoxy thermosets are generally brittle materials in nature, so over the years there was a constant effort to enhance this fracture behavior. The most widely used methods to toughen thermosetting resins are the incorporation of rubber or inorganic particles [**1**]. Rubber toughening can lead to a significant increase in toughness, but this method usually leads to a decrease in the material stiffness and strength, which may be undesirable in many applications. Toughening from inorganic fillers, on the other hand, could result in a more modest improvement of toughness but without significant loss of strength and even with an improvement in modulus **[1-2]**.

Advances in the study of brittle polymers and composite materials suggested the possibility of an early elimination of microcracks to avoid macroscopic damage of the materials. Hence, the concept of self-healing composite materials has been introduced to overcome the difficulty of repairing composite materials, reduce the maintenance cost and frequency and to increase the life in of these materials [**3**]. Self-healing polymers are smart materials, with the ability to autonomically heal the damage without the need for detection or any type of manual intervention. In the recent years, several strategies have been investigated to obtain self-healing polymeric materials [**4-5**]. One of the most studied self-healing systems for polymer composites was inspired by the design of White and colleagues [**6**]. This approach consists on dispersing capsules containing a liquid reactive healing agent and a catalyst or hardener within a polymer matrix. When these capsules are broken by crack propagation, the healing agent is brought out of the capsule, mimicking a biological 'bleeding', and interacts with the catalyst. Thus, the mechanism of healing is triggered and the polymerization of the healing agent leads to the bonding of the crack faces [**6**].

Depending on the type of healing agent employed, it may undergo polymerization by ring opening reaction of encapsulated dicyclopentadiene (DCPD) with a specific

organo-metallic catalyst (Grubbs catalyst) [**6**] dispersed along the polymer matrix or alternatively, the healing agent may be chosen to undergo curing reaction with the chemical agents which may be encapsulated separately [**7**] or as a latent functionality in the polymeric network [**8**].

Although the potential benefits of microcapsule based self-healing systems are numerous, there are certain practical limitations that must be taken into account. One of the critical issues is that the addition of a microencapsulated healing agent in a polymer matrix can significantly alter its processing method and final properties. In order to have feasible self-healing concept, it should not significantly compromise the overall processing and mechanical properties of the polymer matrix. Moreover, transitioning the microcapsule-based self-healing concept from neat resins to structural (fiber reinforced) composites is still challenging and yet to be systematically studied [**9**].

The aim of this work was to evaluate the effect of incorporation of DCPD-loaded microcapsules on the processing conditions and final properties of neat and glass fiber reinforced epoxy matrix. First, microencapsulation of DCPD was performed by using an *in-situ* encapsulation procedure. The matrix material for this work was a diglycidyl ether of bisphenol A (DGEBA) epoxy resin cured with triethylenetetramine (TETA). A key focus of current scientific research was the manufacturing process of microcapsule-loaded epoxy samples, including the selection of the optimal epoxy formulation, mixing process of the capsules and the resin, the degassing stages and curing cycle. Then, the influence of the addition of the microcapsules on the overall thermal, mechanical and fracture properties of the epoxy matrix was analyzed. The next key issue of the current work was the fabrication of fiber reinforced microcapsule-loaded epoxy samples by an adapted hand layup and compression molding process. Finally, the effect of microcapsules addition, as well as their integrity, in the mechanical properties of the composite material was analyzed. It is important to remark that all the processes in this work are described in detail in order to assure the reproducibility of the techniques.

Experimental

Materials

Urea (Anhedra), formaldehyde (40 wt% solution, Biopack), ammonium chloride (Timper) and resorcinol (Biopack) were used as shell forming materials; DCPD (Sigma Aldrich) was the core material. Poly(ethylene-alt-maleic anhydride) (EMA, Sigma Aldrich) with Mw=400000 was used as surfactant.

A diglycidyl ether of bisphenol A resin, DGEBA (DER 383, Dow), with an epoxy equivalent weight of 176 – 183 g/eq and a viscosity of 10025 cps (at 25 ºC) was used in this study. The curing agent was triethylenetetramine (TETA, Distraltec). A monofunctional epoxy diluent (alkylglicidyl ether C12-C14, Distraltec) with an epoxy equivalent weight of 297 g/eq and a viscosity of 8 cps (at 25 ºC) was employed to decrease the viscosity of the epoxy-amine mixture.

A commercially available unidirectional E-Glass fiber fabric (Hexcel) was used with a 90° angle from a Hybon 2032/675 yield roving. These fibers have a yield of 424.6 m/kg, a yield tolerance of 7% and a mean diameter of 13 μm. Fiber surface was sized with silane agent for a better compatibility and better adhesion with the epoxy matrix.

Material synthesis

Synthesis of DCPD-loaded microcapsules

DCPD was microencapsulated with poly(urea-formaldehyde) (PUF) using an in situ emulsion polymerization technique adapted from the literature [**10**]. The encapsulation process was based on a continuously stirred emulsion of DCPD in water which was stabilized by the in situ reaction and condensation of urea and formaldehyde on the emulsion interface. The emulsification step consisted in stirring for 15 min at the reaction speed (600 rpm). After 4 h of reaction time at 55 °C, the PUF particles formed a solid shell and the microcapsules were then filtered, washed with distilled water and dried. Four drying methods were evaluated: 48 h at room temperature; in a convection oven at 35 °C for 24 h; in a vacuum oven at 35 ºC for 24 h; lyophilization (72 h at -45 °C and 100 mTorr).

Preparation of microcapsule-loaded epoxy samples

First, the microcapsules were sieved and dispersed in the epoxy resin, by using 5, 10 and 15 wt.%. The mixture was degassed for 30 min at 60 °C. Then, a stoichiometric amount of TETA was added at room temperature and the suspension was degassed under vacuum for 30 min at 40 °C. After completely removing the bubbles, the mixture was poured in a horizontal mould and then it was left closed at room temperature for 24 h. An aluminum mold coated with Teflon foil was used to facilitate unmolding and a rubber o-ring of 2 mm determined the thickness of the plates. The curing cycle consisted on 1 h at 80 °C, followed by 2 h at 110 °C. The samples were postcured for 30 min at 120 °C.

Preparation of microcapsule-loaded fiber reinforced epoxy samples

Composite samples were manufactured by hand lay-up and compression molding. An aluminum mold coated with Teflon was used to facilitate unmolding and a rubber o-ring of 2 mm which determines the thickness of the plates. First, DGEBA and the diluent were mixed and degassed for 30 min at 80 °C. Then, the microcapsules were added (10 wt. %) and the mixture was degassed for 24 h at 40 °C. Later, a stoichiometric amount of TETA was added at room temperature and the mixture was homogenized. Next, it was proceeded to place into the mold a layer of the reaction mixture and a fiber layer alternately to complete four layers of continuous fibers arranged perpendicularly to each other. Then, the mold

was closed and placed in a PROFLOW AA001PHI press at 80 °C and 10 bar for 30 min. Finally, curing was conducted in a convection oven for 60 min at 80 °C and 120 min at 110 °C, followed by a poscuring cycle which was performed for 30 minutes at 120 °C.

Characterization techniques

The morphology of microcapsules was observed by Scanning Electron Microscopy (SEM, JEOL JSM 6460 LV). The microcapsules were previously mounted on adhesive tape and sputter coated by a thin layer of gold/palladium. Mean diameter and standard deviation were determined from at least 200 measurements.

The core content of the microcapsules was determined by extraction method using acetone as extraction solvent to remove the DCPD from the core.

The thermal stability of the capsules was assessed by thermogravimetric analysis (TGA) in a TA Q200/TGA Q50 thermal analyzer. The microcapsules were heated from 25 to 600 ºC at a rate of 10 ºC/min, under nitrogen atmosphere.

The chemical structure of microcapsules was evaluated by Fourier transform infrared spectroscopy (FTIR) in a Nicolet 6700 Spectrometer equipped with a diamond ATR probe, from 400 to 4000 cm^{-1} wave number regions.

The resin viscosity was measured at 25 ºC by means of a Brookfield DV–II+ cone and plate viscometer with a precision of 2.5 cP.

Three-point bending flexural and fracture tests were carried out in an INSTRON 4467 machine. Flexural tests were done in accordance with ASTMD 790-03 standard over samples of 10 mm × 5 mm × 100 mm at a crosshead speed of 1 mm/min, and the span used was 80 mm. Flexural modulus was determined from the initial slope load-displacement plot. Single-edge notched bend (SENB) specimens were cut out from thick plaques (B = 5 mm). Sharp notches were introduced by sliding a fresh razor blade into a machined slot. Nominal crack to-depth (a/W) was 0.45 < a/W < 0.5, nominal thickness-to depth (B/W) and span-to-depth (S/W) ratios were always kept equal to 0.5, 0.5, and 4, respectively, in accordance with ASTM D 5045 standards. Fracture characterization was carried out in three-point bending at 1 mm/min. Critical stress intensity factor (K_{IC}) values and energy release rate (G_{IC}) values were obtained independently from the critical load and the area under the load–displacement curve up to that load, respectively, following ASTM D 5045-93 standard recommendations. At least three specimens were tested for each sample. The fracture surface of broken specimens was qualitatively analyzed using SEM. Prior to the experiment, the samples were coated by gold/palladium sputter.

Fiber content of composite materials was determined by means of thermal calcination. Small specimens of approximately 5 g were placed in muffle furnace set at 575 °C for 5 h, leaving only the glass fiber as a residue after heating. The glass fiber content was calculated from the masses of each specimen before and after calcination.

Differential Scanning Calorimetry (DSC) thermograms were recorded using a TA-Q2000 calorimeter. The tests were performed at a scanning rate of 10 ºC/min from room temperature to 250 ºC in nitrogen flow. Glass transition temperature (*Tg*) of each sample was determined as the midpoint of the temperature range, bounded by the tangents to the two flat regions of the heat flow curve.

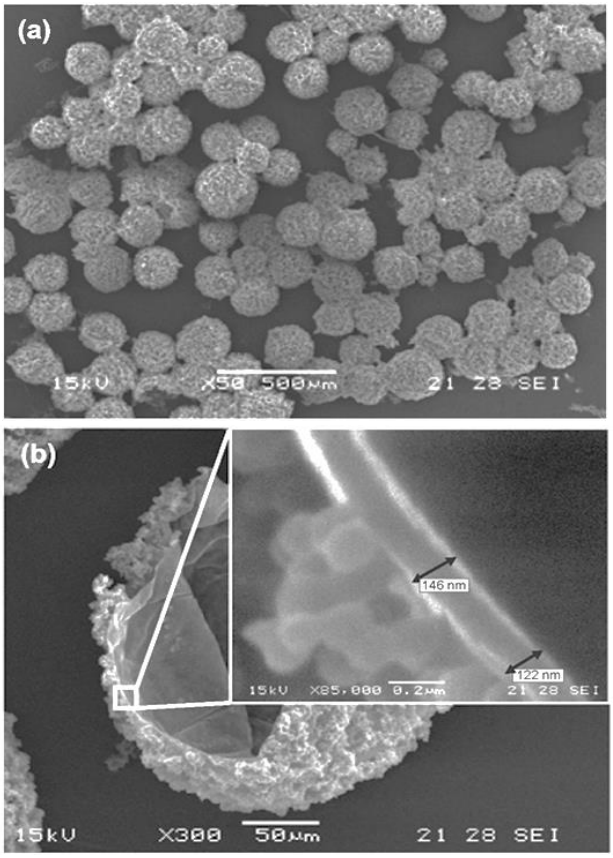

Fig 1. SEM micrographs of: (a) PUF/DCPD MCs; (b) PUF shell of a broken MC.

Results and discussion

Microcapsules characterization

One of the key features for the effectiveness of the healing system is the microcapsules (MCs) synthesis. In oil-in-water emulsion in situ polymerization, DCPD is emulsified in an aqueous solution containing the surfactant (EMA), urea and formaldehyde (as well as small quantities of ammonium chloride and resorcinol). Polymerization of the urea and formaldehyde takes place in the water and the newly formed polymer then deposits at the interface between the suspended DCPD droplets and the aqueous phase, forming the shell of the MCs [**11**]. The MC size can be controlled by the agitation rate during the synthesis [**10**]. In this work, the stirring rate was adjusted to 600 rpm to produce spherical MCs of an average diameter of 150 μm and a core content of 62 wt.%. The drying method of the MCs was an important aspect in the quality of the resulting product. The only method that provided a free-flowing powder was

lyophilization. With the rest of the procedures, the MCs agglomerated so they were not viable to obtain a powder-like product.

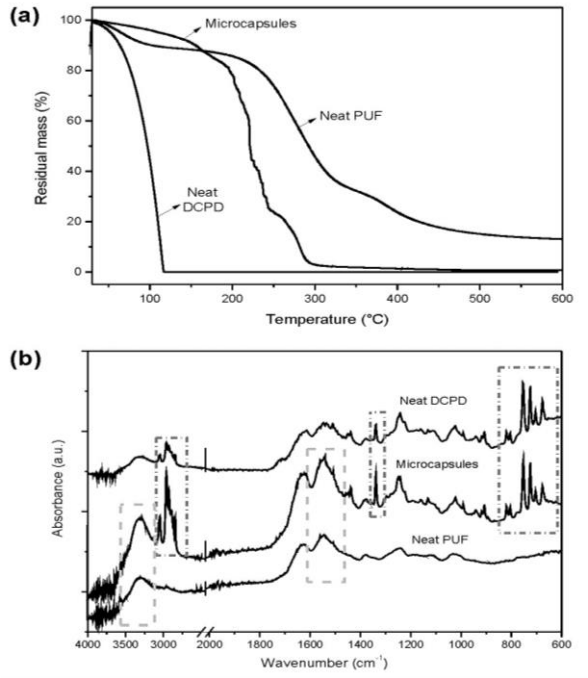

Fig 2. FTIR (a) and TGA (b) characterizations of PUF/DCPD MCs compared with neat DCPD and PUF.

SEM micrograph in **Fig. 1a** shows the presence of high quality spherical MCs in the lyophilized powder. Moreover, the PUF shell wall presented an inner smooth and compact surface free of voids and a rough outer surface (**Fig. 1.b**). The thickness of the smooth part of the wall was 134 ± 8 nm. This is in accordance with the results reported by other authors [**10**]. In order to have a successful self-healing performance, it is important to synthesize MCs with rough surface morphology to assure a good mechanical adhesion with de polymer matrix [**12**]. Besides morphological examination, FTIR spectra of the MCs revealed the presence of characteristic peaks of both DCPD and PUF [**13**], which are marked with rectangles in **Fig. 2a**. This confirms that DCPD was successfully encapsulated by PUF. Additionally, when polymer composites are thermally cured, the embedded MCs (and also the catalyst) have to experience heat impact [**14**]. Therefore, their thermal stability must be analyzed. TGA measurements (shown in **Fig. 2.b**) evidenced that the MCs were thermally stable up to 155 °C.

Microcapsule-loaded epoxy samples

First, it is very important to study the viscosity of each DGEBA/TETA/MCs mixture to facilitate the mixing process and casting into the mold. Thus, the first step of this work was to determine the diluent content required to achieve similar viscosity values with different contents by weight of MCs (5, 10 and 15 wt.%). **Table 1** evidences that higher diluent amounts were needed for increasing capsule contents.

Table 1. Viscosity values (at 25 ºC) of DGEBA/TETA mixtures with different diluent and MC contents.

Diluent content (wt. %)	*MCs content (wt. %)*	*Viscosity (cp)*
0	5	1765 ± 15
3	10	2478 ± 15
5	15	2243 ± 17

Table 2 resumes thermal, mechanical and fracture properties of fully cured control and MCs-loaded epoxy samples. MCs were homogenously dispersed in all cases and no trapped air bubbles were observed in the resulting samples, as a consequence of several degassing steps. Higher chain mobility with increasing amounts of diluent content due to lower crosslink density of epoxy/amine system may be responsible for the shift to lower *Tg* values of control samples [**15**]. Moreover, the presence of MCs practically did not affect the *Tg* values of the materials.

The effect of the addition of DCPD-loaded MCs on the mechanical properties of the epoxy matrix is of crucial importance, as the advantages of introducing self-healing capability should not result in detriment of the application. However, from the observation of **Table 2**, it can be deduced that the introduction of MCs resulted in a reduction of the flexural properties compared with the neat epoxy samples.

In fracture tests, the epoxy matrix and the composites displayed almost linear elastic behavior and failed by unstable crack growth. Therefore, single initiation values of the fracture parameters were obtained. The addition of MCs also led to a proportional decrease in the critical stress intensity factor, K_{1C}, and fracture energy, G_q. This effect could be associated to a poor epoxy-MC adhesion,

Table 2. Thermal, flexural and fracture properties of the samples.

MCs content (wt. %)	Diluent content (wt. %)	Tg (ºC)	Maximum flexural strenght (MPa)	Flexural modulus (GPa)	K_{1C} (MPa $m^{1/2}$)	G_q (kJ/m^2)	
						Measured	Calculated
0	0	131	124 ± 9	2.91 ± 0.11	0.525 ± 0.014	1.70 ± 0.40	1.09
0	3	124	138 ± 3	2.94 ± 0.04	0.552 ± 0.018	1.60 ± 0.40	0.96
0	5	119	120 ± 4	2.83 ± 0.04	0.558 ± 0.012	1.80 ± 0.50	1.26
5	0	127	54 ± 4	1.15 ± 0.02	0.425 ± 0.010	1.20 ± 0.20	1.38
10	3	123	58 ± 2	1.66 ± 0.03	0.407 ± 0.007	1.11 ± 0.06	0.82
15	5	115	60 ± 6	1.56 ± 0.07	0.351 ± 0.013	0.90 ± 0.30	0.57

resulting that the microcapsules acted like voids. **Fig. 3** shows SEM micrographs of the fracture surface of SENB for the epoxy specimen with 10 wt.% MC. It can be observed that some MCs were broken, whereas others were pulled out by crack propagation, possibly because the strength necessary to break the MC was higher in comparison to the MC-epoxy interfacial strength.
G_{IC} can also be calculated from fracture toughness values as follows:

$$G_{IC} = K_{IC}^2 / E (1-\upsilon^2) \quad (1)$$

where E is the modulus of elasticity and υ is the Poisson's ratio of the polymer, taken to be 0.35 [**16**].

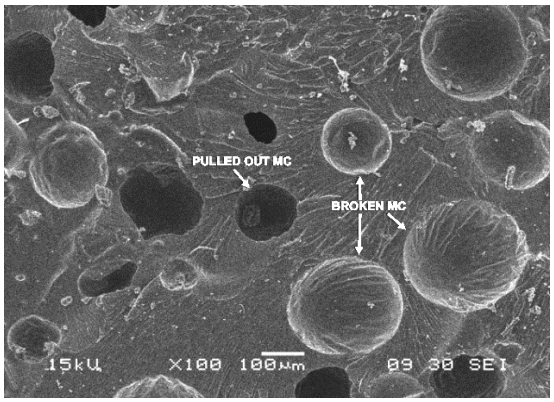

Fig. 3. SEM micrograph of a fractured epoxy specimen with 10 wt.% MCs.

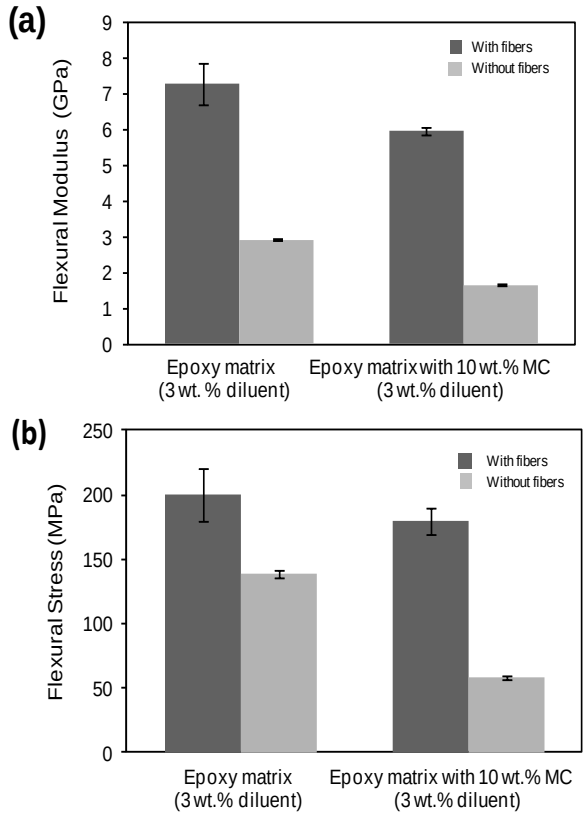

Fig. 4. Comparison of (a) flexural modulus and (b) flexural strength of fiber reinforced composites with and without MCs.

As it can be clearly seen in **Table 2,** there are differences among the calculated and the measured energy release rate parameter values being measured; values are always higher than calculated ones. This is probably because of the existence of some dissipation mechanisms such as plastic void growth and matrix plastic deformation that are not accounted in linear elastic fracture mechanics (LEFM). It should also be noted that all composites exhibited fracture toughness values significantly lower than that of the matrix, due to the low adhesion between matrix and the MC surface. Typical features of the fracture of brittle thermosets are clearly observed in SEM micrograph of **Fig. 3**.

They are characterized by relatively smooth and glassy fracture surfaces with no signs of large-scale plastic deformation [**16**]. Feather markings can also be seen. They can be identified as apparent steps and changes of level of the crack clearly visible near the broken MC in **Fig. 3**. They are caused by crack forking because of the excess of energy associated with the relatively fast crack growth in a brittle material [**2**]. This is in agreement with the low value of fracture toughness obtained for the matrix, which is typical of brittle polymers and similar systems found in literature (K_{IC}= 0.59 MPa $m^{1/2}$) [**16**].

Fiber-reinforced composites with MCs

The last part of the study was focused on improving the mechanical performance of the materials through hybridization. As self-healing composites are most likely to be applied in high-performance applications, glass fiber was selected as reinforcement. Therefore, once optimized the processing of the matrix with MCs, unidirectional woven glass fibers were added to develop a composite material. Samples were prepared by hand layup followed by compression molding and the processing parameters were selected so as to ensure a good dispersion of MCs along the material and to avoid their rupture when the sample was compressed before curing. The materials resulted in 32 wt. % fiber contents.

The mechanical properties of the composites were analyzed by a bending test. In **Fig. 4**, comparative graphs are shown with the average mechanical properties of the matrix and fiber reinforced composite specimens, with and without 10 wt.% MCs. As it can be seen, the addition of MCs caused a detriment on the mechanical properties of the composites. However, the change in the properties because of the presence of MCs was lower than for the case of the same material without fibers (analyzed before), due to the fact that mechanical properties of the composites are given mainly by the continuous reinforcement. As seen in **Fig. 4.a**, the addition of 32 wt. % fibers as reinforcement to the matrix increased flexural modulus in 250 %, and in the case of specimens with MCs, the flexural modulus increased in approximately 360 %. As expected, the addition of woven fiber increased the flexural modulus of the specimens compared with their respective matrix. Furthermore, when comparing the flexural strength of each composite

regarding its original matrix, can be seen that in the case of the epoxy matrix, the increase was approximately 150 %, whereas in the case of matrix with MCs it was increased approximately 310 % (see **Fig. 4.b**). This can be attributed, as in the case of the modulus values, to the fact that mechanical properties of the composite depend mainly on the properties of reinforcement rather than the properties of the matrix.

Lastly, the influence of compression molding technique in the integrity of the MCs was evaluated. Tested specimens surface were observed by SEM microscopy and it was verified that the adhesion between the fibers and the matrix was good because no "pull-out" was registered (**Fig. 5 a,b**).

In **Fig. 5a** it can be seen that the fibers were cut over the crack plane. Moreover, in **Fig. 5.b** cut fibers and some intact MCs and others broken by the passage of the crack can be observed. This indicates that the MCs did not break during the pressing process of the specimens.

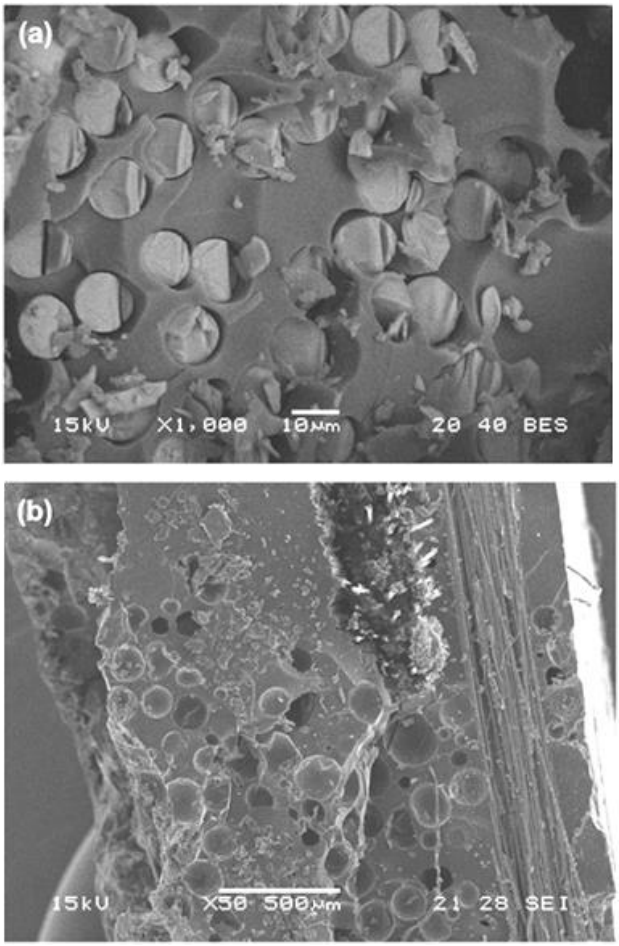

Fig. 5. SEM micrographs of the fracture surface of neat fiber reinforced composite (a) and 10 wt.% MCs fiber reinforced composite (b).

Conclusion

In this work, PUF/DCPD microcapsules were firstly synthesized by adapting the emulsion based urea-formaldehyde in-situ polymerization technique from the bibliography. Spherical and stable DCPD-loaded MCs were obtained as a free-flowing powder after lyophilization process. Then, the processing of epoxy/DCPD-loaded MCs specimens was optimized by degassing the final mixture for long times and using a suitable viscosity to allow proper casting, resulting in good distribution of MCs within the matrix. Specimens with different loadings of MCs (5, 10 and 15 wt. %) were characterized according to their mechanical properties in bending (strength and modulus) by three-point bending tests, as well as its fracture properties (K_{IC} and G_q) by fracture tests (plane strain). It was concluded that the MCs caused a decrease mechanical and fracture properties of the matrix since they had poor adhesion to the matrix and thus acted as defects. However, it was possible to observe some microcapsules broken by the crack propagation, so it is still possible to use this material for applications with self-healing capabilities, but the adhesion of the microcapsules to the matrix should be improved to optimize efficiency in the future repair and mechanical and fracto-mechanical properties.

Finally, E-glass fiber reinforced composite materials were successfully manufactured through hand layup followed by compression molding. It was observed that the addition of a 32 wt.% of glass fibers to the epoxy matrix, with and without 10 wt. % of MCs, resulted in increased flexural mechanical properties (modulus and strength). Appropriate fabrication technique was confirmed since MCs resisted molding and handling of the mixture as observed in SEM images.

Future work regarding the study of the self-healing capability of fiber reinforced epoxy materials with DCPD-loaded MCs and Grubbs catalyst will be performed.

Acknowledgements

This work was supported by funding of CONICET, UNMdP and ANPCyT (Project FSNano 004).

Author's contributions

Authors have no competing financial interests.

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