University of Groningen

Development of self-healing epoxy composites via incorporation of microencapsulated epoxy and mercaptan in poly(methyl methacrylate) shell

Ahangaran, Fatemeh; Hayaty, Mehran; Navarchian, Amir H.; Pei, Yutao; Picchioni, Francesco

Published in:
Polymer testing

DOI:
[10.1016/j.polymertesting.2018.11.041](https://doi.org/10.1016/j.polymertesting.2018.11.041)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Ahangaran, F., Hayaty, M., Navarchian, A. H., Pei, Y., & Picchioni, F. (2019). Development of self-healing epoxy composites via incorporation of microencapsulated epoxy and mercaptan in poly(methyl methacrylate) shell. *Polymer testing*, 73, 395-403. <https://doi.org/10.1016/j.polymertesting.2018.11.041>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Material Properties

Development of self-healing epoxy composites via incorporation of microencapsulated epoxy and mercaptan in poly(methyl methacrylate) shell

Fatemeh Ahangaran^{a,b,c}, Mehran Hayaty^{a,*}, Amir H. Navarchian^b, Yutao Pei^d,
Francesco Picchioni^c

^a Department of Applied Chemistry, Malek-ashtar University of Technology, Isfahan, 83145/115, I.R. Iran

^b Department of Chemical Engineering, Faculty of Engineering, University of Isfahan, Isfahan, 81746-73441, I.R. Iran

^c Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747, AG, Groningen, The Netherlands

^d Department of Advanced Production Engineering, Engineering and Technology Institute Groningen, University of Groningen, Nijenborgh 4, 9747, AG, Groningen, The Netherlands

ARTICLE INFO

Keywords:

Epoxy composite

Healing agent

PMMA microcapsule

Mechanical properties

Self-healing behavior

ABSTRACT

Self-healing composites based on epoxy resin containing poly(methyl methacrylate) (PMMA) microcapsules filled with healing agents were prepared. The effect of healing agents microcapsules on mechanical properties and self-healing behavior of epoxy composites were investigated in this work. Epoxy and mercaptan as curing agent were microencapsulated in PMMA shell as two-component healing agent through internal phase separation method, and then, epoxy composites containing 2.5, 5, 7.5 and 10 wt% of healing agent microcapsules were prepared. The fracture toughness and healing efficiency of these composites were measured using a tapered double cantilever beam (TDCB) specimen. The results indicated that about 80% healing efficiency was achieved with 10 wt% PMMA microcapsules at room temperature after 24 h. The tensile strength of the epoxy with 2.5 wt % PMMA microcapsules increased initially and then decreased gradually with increasing microcapsules content up to 10 wt% PMMA microcapsules. DSC results also indicated that this system has good potential for spontaneous self-healing performance at room temperature.

1. Introduction

Polymer matrix composites are widely used in tremendous engineering fields because these materials are capable to provide advantages including improved mechanical, electrical, chemical, or thermal properties compared to the pure composite matrix [1]. Epoxy resins are one of the polymers used as high performance matrix in composites but microcracking of these composites is a critical problem during their service in structural applications. Microcracks are deeply occurred within a structural component and it is difficult to detect and repair by conventional methods [2]. Self-healing materials can repair microcracks without any detection techniques or a special manual intervention, and offer tremendous potential for providing long-lived composites, reduction the cost associated with repair and maintenance, and improving the durability and reliability of materials [3]. Self-healing materials have been developed through encapsulation of healing agents in microcapsules [4–6], hollow fibers [7,8], and microvascular networks [9,10]. Microcracks propagate through the material and encounter healing agent carriers, easily cause their rupture,

thus release the healing agents along the crack surface react together and heal the damaged region [11].

Two-component healing agent system was developed by several authors, which consists of microencapsulated polymerizable component and its hardener. In order to meet criteria of self-healing including high flowability and rapid consolidation, the using of low viscosity and highly active healing agents is very important [3]. Epoxy composites containing healing agent microcapsules have been reported in several studies [3,12–15]. Brown et al. encapsulated dicyclopentadiene (DCPD) in PUF shell and used to repair the damage in epoxy matrix [12]. Yuan et al. microencapsulated epoxy and mercaptan using poly(melamine formaldehyde) (PMF) as shell and prepared self-healing epoxy composite [3,13]. Mangun et al. prepared high temperature cured self-healing epoxy composite via incorporating poly(urea formaldehyde) (PUF) microcapsules filled with poly(dimethyl siloxane) (PDMS) resin and separate poly(urethane) (PU) microcapsules containing an organotin catalyst [14]. Li et al. investigated the self-healing performance of epoxy composite by using microencapsulation of high viscosity epoxy resin and poly(ether amine) curing agent in poly(methyl methacrylate)

* Corresponding author.

E-mail address: mehayaty@mut-es.ac.ir (M. Hayaty).

<https://doi.org/10.1016/j.polymeresting.2018.11.041>

Received 22 August 2018; Received in revised form 13 November 2018; Accepted 26 November 2018

Available online 28 November 2018

0142-9418/ © 2018 Elsevier Ltd. All rights reserved.

Fig. 1. TDCB composite sample containing 10 wt% PMMA microcapsules (weight ratio of the epoxy- and mercaptan-filled microcapsules was 1:1).

(PMMA) shell [15,16].

In this work, self-healing system is employed low-viscous highly active epoxy as the polymerizable component and mercaptan in conjunction with tertiary amine catalyst as hardener. Epoxy has good adhesion to many materials and is an ideal candidate for versatile healing agent. The mercaptan curing agent is very active and many polymers are not suitable for encapsulating it, PMMA was chosen which is inert toward mercaptan as the shell material. PMMA also has high chemical stability, good mechanical properties, low strain at break, and excellent compatibility with the epoxy matrix [15]. In our previous works, for the first time, low viscosity epoxy and mercaptan were encapsulated in PMMA and investigated the PMMA microcapsules properties [4,17,18]. The effects of processing parameters on the encapsulation of low viscosity self-healing agents in PMMA shell were investigated [4]. The morphology of microcapsules filled with different self-healing agents (low viscosity epoxy, mercaptan, and cycloaliphatic amine), in separate PMMA shells investigated experimentally and theoretically in various emulsion systems [17]. Then, in the next work, the elastic modulus and hardness of PMMA microcapsules containing epoxy and mercaptan as healing agents were investigated using nanoindentation technique [18]. To the best of our knowledge, the self-healing and mechanical properties of epoxy composite based on encapsulated epoxy and mercaptan

curing agent in PMMA shell have not yet been reported in the literature. Here, the self-healing performance of epoxy- and mercaptan-filled PMMA microcapsules, which were embedded in epoxy matrix were investigated. In addition, the influence of the addition of the PMMA microcapsules on the mechanical properties of the epoxy was also studied.

2. Experimental

2.1. Materials

Epoxy prepolymer (EC157) as polymerizable component of the healing agent was purchased from Elantas Co., Italy. Pentaerythritol tetrakis (3-mercaptopropionate) (PETMP) was used as the hardener for healing agent and was purchased from Sigma Aldrich, USA. For the composite matrix, Epikote™ 828 as the matrix resin and Epikure™ F205 as the curing agent were purchased from Hexion Co., The Netherlands. PMMA ($M_w = 550,000$ g/mol) as capsule shell was purchased from Alfa aesar Co., USA. Dichloromethane (DCM) was purchased from Acros Organics Co., Belgium. Benzyl dimethylamine (BDMA) as catalyst for healing reaction, methanol as solvent, sodium dodecyl sulfate (SDS), and cetyltrimethylammonium bromide (CTAB) as surfactant were purchased from Sigma Aldrich Co., USA. All materials were used as received without further purification.

2.2. Microencapsulation of healing agents in PMMA shell

Epoxy- and mercaptan-loaded PMMA microcapsules were separately prepared by dissolving 4 g of healing agent and 4 g PMMA in 120 ml of DCM as oil phase. In the encapsulation process of mercaptan, 0.4 g of BDMA as catalyst for polymerization of epoxy prepolymer with mercaptan was also added to the oil phase. The resultant oil phase was added to aqueous phase (200 ml of 1 wt% emulsifier solution) under high mechanical mixing rate, 1000 rpm at room temperature for 30 min to obtain oil in water emulsion (O/W). In this procedure, CTAB and SDS were used as emulsifier for microencapsulation of epoxy and mercaptan, respectively. The resultant emulsion was dispersed into 300 ml of 1 wt% aqueous emulsifier solution under stirring. After completely evaporation of DCM, healing agent microcapsules were formed. PMMA microcapsules containing healing agent were filtered and washed several times with methanol and distilled water and dried at room temperature.

Fig. 2. FTIR spectra of (a) neat epoxy, neat PMMA and epoxy/PMMA microcapsules, and (b) neat mercaptan, neat PMMA and mercaptan/PMMA microcapsules.

Fig. 3. ESEM micrographs of (a) epoxy-loaded PMMA microcapsules and (b) mercaptan-loaded PMMA microcapsules.

Fig. 4. Size distributions of epoxy- and mercaptan-loaded PMMA microcapsules.

Fig. 5. Tensile stress-strain curves of the epoxy composites with various PMMA microcapsules content.

Fig. 6. (a) Tensile strength and (b) Young's modulus of the epoxy composites with various PMMA microcapsules content.

Fig. 7. SEM images of cross-section of epoxy composite with 5 wt% epoxy contained microcapsules and 5 wt% mercaptan contained microcapsules a): $\times 1000$, b) $\times 2000$.

2.3. Fabrication of self-healing epoxy composites

Pure epoxy specimens were prepared by mixing 100 parts Epikote™ 828 and 58 parts of Epikure™ F205 as hardener, and self-healing epoxy composites were also prepared by mixing various amounts of 2.5, 5, 7.5 and 10 wt% of epoxy- and mercaptan-loaded PMMA microcapsules with the aforesaid Epikot™ 828/Epikure™ F205 mixture. The weight ratio of epoxy- and mercaptan-filled microcapsules in all the self-healing specimens was 1:1. The pure epoxy or composite specimens were degassed, poured into silicon rubber molds with tapered double cantilever beam (TDCB) geometry (Fig. 1) and dumbbell shape and cured for 24 h at room temperature, followed post-cured at 80 °C for 1 h.

2.4. Characterization

2.4.1. Microcapsules characterization

Chemical structure of healing agent microcapsules were studied using Fourier transform infrared (FTIR-ATR) spectroscopy (IR Tracer-100, Shimadzu, Japan) in the range of 500–4000 cm^{-1} , to identify the functional groups. The curing reaction between the two components of the healing agents released from ruptured PMMA microcapsules was investigated using dynamic differential scanning calorimetry (DSC Pyris 1, Perkin Elmer Co., USA). The heating rate for the dynamic measurements was adjusted to 10 °C min^{-1} from 25 to 150 °C under nitrogen gas.

The size and morphology of the healing agent microcapsules and the fracture surface of self-healing composites were taken using environmental scanning electron microscopy (ESEM) at different magnifications (Philips ESEM-XL30, the Netherlands). The mean size of microcapsules was measured using dynamic light scattering (DLS) (Brookhaven Instrument Co., USA).

In order to determine the core content of both the epoxy- and mercaptan-loaded PMMA microcapsules, the extraction method by Soxhlet with methanol as solvent was employed as described in our previous work [4]. The yield of encapsulation of healing agent with PMMA shell, α , was defined by determining the ratio of the collected capsules mass, w , to the total mass of healing agent and PMMA feed [4].

$$\alpha = \left[\frac{W}{W_{\text{core}} + W_{\text{shell}}} \right] \times 100\% \quad (1)$$

2.4.2. Mechanical and self-healing studies

The tensile properties were measured using a servo-hydraulic material testing system (MTS 810, MTS System Corporation, Minneapolis, MN) with a speed of 1 mm/min. For each sample five specimens were tested and an average value was reported. The tensile samples of epoxy

and self-healing composites were prepared according to ASTM D638, type II specimen.

Self-healing performance of samples was evaluated according to fracture test on TDCB geometry that proposed by White et al. [19]. The TDCB samples were prepared with short groove length to produce less crack face separation. The pre-crack was created into the groove of TDCB samples by inserting a fresh razor blade and gently tapping into the mold notch starter. The fracture test was carried out under the displacement control using a 5 $\mu\text{m s}^{-1}$ displacement rate at room temperature. The specimens were fractured only to the end of groove and then the cracked specimens were unloaded, allowing the crack face to come back into contact and self-healed at room temperature for 24 h. The healed specimens were tested again following the above procedure. The healing efficiency for each sample was averaged from three specimens.

3. Results and discussion

3.1. Characteristics of PMMA microcapsules

Fig. 2a shows the FTIR spectra of neat epoxy, neat PMMA and PMMA microcapsules containing epoxy. The FTIR spectrum of epoxy shows absorption peaks at 912 and 1236 cm^{-1} that indicate the C-O deformation band and stretching vibration of the oxirane group, respectively [20]. For the neat PMMA, it can be seen that there is a distinct absorption band at 1141 cm^{-1} that is due to O-CH₃ stretching vibration. The absorption peaks at 1139 and 1238 cm^{-1} can be attributed to C-O stretching vibration and the C-O-C single band stretching vibration, respectively. The band at 1720 cm^{-1} shows the presence of C=O group. The C-H stretching absorption peaks of -CH₂ and -CH₃ appeared at 2949 and 2991 cm^{-1} , respectively [21]. The FTIR spectrum of epoxy/PMMA microcapsules indicates the characteristic peaks of neat epoxy and neat PMMA, confirming the successful microencapsulation of epoxy with PMMA without occurring any chemical reactions.

Fig. 2b indicates the FT-IR spectra of the neat mercaptan, neat PMMA and mercaptan-loaded PMMA microcapsules. The spectrum of PETMP shows stretching vibration of C-O at 1145 cm^{-1} , stretching of C=O at 1718 cm^{-1} and characteristic stretching peak of S-H at 2567 cm^{-1} [11]. The C-H stretching vibration peaks of methylene group (-CH₂) appeared at 2902 and 2949 cm^{-1} . All the characteristic peaks of both neat mercaptan and neat PMMA appeared also on the FTIR spectrum of the PETMP/PMMA microcapsules.

The thermal stability of healing agents, PMMA and microcapsules were studied using thermogravimetric analysis.

ESEM micrographs of the encapsulated epoxy and mercaptan in

Fig. 8. Typical load-displacement curves for TDCB fracture specimens of (a) pure epoxy, (b) epoxy with 2.5 wt% microcapsules, (c) epoxy with 5 wt% microcapsules, (d) epoxy with 7.5 wt% microcapsules, and (e) epoxy with 10 wt% microcapsules.

Fig. 9. Influence of healing agent microcapsules concentration on fracture toughness of virgin and healed epoxy composites.

Fig. 10. ESEM micrograph of crack propagation around PMMA microcapsule before healing.

PMMA shell are presented in Fig. 3 (a and b). The healing agent microcapsules are formed in spherical shape and with relatively smooth surface morphology. ESEM images of PMMA microcapsules indicate just a unimodal size distribution with different mean diameter as observed in Fig. 4. In the previous studies, it is suggested that the most important process parameters influencing the size and size distribution of capsules are the composition of continuous organic phase, the volume ratio of the internal oil phase, the viscosity of the oil phase, the type and concentration of surfactant, and agitation rate (shear rate) [22–24]. It is reported that the size and size distributions of microcapsules is affected by the variation in fluid flow around the propeller and away from that. In the vicinity of the propeller blades, the shear rate is higher than away from that and many smaller microeddies exist that leads to the formation of smaller microcapsules in suspension system [12]. In Fig. 4, similar narrow size distributions are seen for both healing agent microcapsules. The mean size of epoxy- and mercaptan-filled microcapsules were measured 21 and 25 μm , respectively. The encapsulation yield of epoxy and mercaptan with PMMA shell were

determined 68% and 75%, respectively. As explained in experimental section, the core content of PMMA microcapsule can be measured by extraction method using methanol as solvent. The core content of PMMA microcapsules containing epoxy and mercaptan were determined 35% and 33%, respectively.

3.2. Mechanical properties

The influence of microencapsulated epoxy and mercaptan curing agent on mechanical performance of epoxy matrix is worth being understood. The tensile properties of self-healing composites were measured as a function of the healing agent microcapsule concentration. Fig. 5 represents the typical tensile stress-strain curves of the pure epoxy matrix and self-healing epoxy composites loaded epoxy- and mercaptan-filled microcapsules. The ultimate tensile strength of filled epoxy composites with dual-component microcapsules according to microcapsule concentration are indicated in Fig. 6a. The reported values of tensile strength reflect the mean value of five measurements with the corresponding standard deviation. The tensile strength of the pure epoxy matrix was measured 58.02 MPa. It is observed that the tensile strength of epoxy composite with incorporation 2.5 wt% of PMMA microcapsules increases to 59.21 MPa and then it decreases to 47.30 MPa with further increasing the concentration of PMMA microcapsules up to 10 wt%. The decreasing trend in tensile strength is in accordance with results obtained in previous studies about the effect of healing agent microcapsules on tensile properties of self-healing epoxy composites [3,15,25]. Yuan et al. reported a continuous trend of reduction in the tensile strength of epoxy composites with embedded PMF microcapsules containing epoxy and mercaptan curing agent [3]. In addition, Li et al. showed the initially increasing in tensile strength of self-healing composite containing epoxy- and amine-PMMA microcapsules compared to pure epoxy matrix can be due to the increased toughness by incorporating thermoplastic PMMA shell [15]. The decrease of the tensile strength of the self-healing epoxy composites can be explained in two aspects. On one hand, the microcapsules filled with healing agents can be treated as defects at the cross-section of composites. On the other hand, the interface between the microcapsule shell and the epoxy matrix is the weaker area, which also deteriorate the properties upon the tensile loading [25].

The Young's modulus of the epoxy composite filled with healing agent/PMMA microcapsules was measured as the slope of stress-strain curve at strain below 1%. Fig. 6b represents the trends of the Young's modulus with respect to the increase of the total concentration of the epoxy and mercaptan microcapsules at the equal weight ratio. It is clear that the reduction tendency of Young's modulus was also observed for epoxy composites with dual-component microcapsules compared to pure epoxy. The Young's modulus decreases from 2.6 to 1.9 GPa for the composite by 10 wt% compared to the pure epoxy. Yuan et al. also showed the Young's modulus of epoxy composites decreased by incorporation of PMF microcapsules containing epoxy and mercaptan in epoxy matrix [3]. In the current study, this can be due to the incorporating of thermoplastic PMMA shell in the thermoset epoxy matrix, which reduces the Young's modulus of matrix. Also, the weak interfacial adhesion between PMMA shell and epoxy matrix may cause the microcapsule surface to slip on its position within the matrix that results in a reduction in the Young's modulus of composite.

Fig. 7 represents ESEM micrographs of the cross-section of tensile specimens filled with 10 wt% of both types of PMMA microcapsules. It is clear that the PMMA microcapsules breakage and pull-out occurring in epoxy matrix. The interfacial voids between the epoxy matrix and PMMA shell of microcapsules are due to pulling-out the microcapsules from the epoxy matrix during the tensile test. From the ESEM micrographs it is clear that the mean thickness of PMMA shell of microcapsules is about 2.5 μm .

Fig. 11. Influence of healing agent microcapsules content on healing efficiency of epoxy composites.

3.3. Self-healing performance

The effect of the concentration of PMMA microcapsules in the range of 2.5–10 wt% on the healing efficiency of epoxy composites were evaluated using fracture test. According to the previous studies on self-healing composite using epoxy and mercaptan as healing agents, in this study a constant weight ratio of epoxy and mercaptan microcapsules of 1:1 was used for the preparation of self-healing composites [3,15]. The healing efficiency using the TDCB geometry was measured with the same parameters for comparison the virgin and healed samples. The healing efficiency, η , is defined as the ratio of fracture toughness of healed (K_{IC}^{Healed}) specimens to that of virgin (K_{IC}^{Virgin}), as [26]:

$$\eta = \frac{K_{IC}^{Healed}}{K_{IC}^{Virgin}} = \frac{P_C^{Healed}}{P_C^{Virgin}} \quad (2)$$

Where P_C^{Healed} and P_C^{Virgin} are healed peak load and virgin peak load in the load-displacement curve of fracture tests, respectively. In this investigation, as several peaks may appear on the load-displacement curve of healed samples, the average of all the peaks was determined for the calculation of healing efficiency [27]. Typical

load-displacement curves of the original fracture and healed fracture for a pure epoxy matrix and epoxy composites containing 2.5 to 10 wt% healing agent microcapsules are given in Fig. 8(a–e). A linear (brittle) fracture behavior was observed in the initial test of virgin test for all samples. The pure epoxy specimens does not demonstrate any healing capability after the second fracture test at room temperature after 24 h. Fig. 8(b–e) display that the load increased in lower displacement for the healed samples than the virgin samples. It can be probably due to the bonding material in healed regions not only heals the cracks but also provides the healed sites with higher cracking resistance than the virgin samples [3]. The healed composite also exhibit unstable stick-slip cracks propagation in their load-displacement curves (Fig. 8(b–e)). This may be due to the fact that the cured epoxy-mercaptan regions starts to tear away from the crack plane in crack propagation way, and distinct healed peaks appear in load-displacement curves [28]. In the other words, after the healed material debonded, the curve loads up and the additional energy must have been consumed during fracture [3]. The slope of load-displacement curves for all samples is gentle after the healing performance (Fig. 8(b–e)). This can be attributed to the lower modulus of the healed epoxy resin (EC 157) compared to the epoxy resin of matrix (Epikote™ 828) [29].

The influence of the healing agent microcapsules on the original fracture toughness, K_{IC} , was investigated, as explained in Fig. 9. When the concentration of microcapsules increased to 10 wt%, the fracture toughness increased gradually from 1.8 to 2.0 MPam^{1/2}. The virgin epoxy composites are tougher than the unfilled epoxy and healed epoxy composites. The dependence of fracture toughness of healed self-healing specimens on microcapsule content also follows similar increasing trend in the range of 0–1.6 MPam^{1/2} from pure epoxy to epoxy with 10 wt% healing agent microcapsules. The toughening effect coincides with the observation in other studies of self-healing composite containing microcapsules [3,13,27]. It is suggested that the healing agents not only heals the cracks but also provides the damaged sites with higher fracture toughness [3]. Toughening of epoxy composites due to the addition of microcapsule filled with liquid healing agent can be explained by the crack pinning mechanism. Crack pinning typically occurs in polymers with well-bonded, high stiffness particles, such as silica [30]. This mechanism also reported in self-healing composite containing polymeric microcapsules [31]. It is suggested that the crack pinning around the broken microcapsules increases the resistance against the growth of the crack and as a result the fracture toughness increases. ESEM micrograph from the fracture surface of PMMA microcapsules embedded in epoxy specimen before healing are shown in Fig. 10. In this image, the crack pinning mechanism around the broken PMMA microcapsule is clearly observable.

Fig. 12. ESEM micrographs of (a) crack propagation direction in PMMA microcapsules embedded in epoxy matrix, and (b) fracture surface of epoxy filled with dual PMMA microcapsules after healing (second fracture test).

Fig. 13. DSC curves for (a) epoxy (EC 157)/mercaptan (PETMP), (b) epoxy/mercaptan (PETMP)/BDMA, (c) epoxy matrix, (d) epoxy with 2.5 wt% microcapsules, (e) epoxy with 5 wt% microcapsules, (f) epoxy with 7.5 wt% microcapsules, and (g) epoxy with 10 wt% microcapsules.

As Fig. 8 has indicated the crack healing ability of the healing agents, the influence of healing agent's concentration on healing efficiency should be known. Fig. 11 shows at a constant weight ratio of epoxy and hardener microcapsules of 1:1, the healing efficiency of epoxy composites increased markedly with an increase in microcapsules content from 2.5 to 10 wt%. The maximum healing efficiency has been obtained 80.14% with the 10 wt% of healing agent microcapsules. Clearly, the healing effect is related to the quantity of the healing agents released by the broken microcapsules on the fracture surface. This rapid increase in the healing efficiency results from the enough released epoxy and hardener to fill the microcrack space [32]. The dual-component microcapsules embedded in epoxy system provided enough epoxy and mercaptan for curing and for promoting the bonding of the new thermoset epoxy to the original matrix interface. It is worth noting that healing ability of a self-healing epoxy composite is determined by the reaction between the healing agents. In this work, the epoxy-mercaptan pair would hardly react together without proper catalysis. The catalyst reaction of epoxy-mercaptan using a tertiary amine catalyst can be considered as addition polymerization mechanism [3].

Fig. 12a indicates the crack propagation direction through the microcapsules embedded in epoxy matrix. During the crack propagation, PMMA shell of microcapsule ruptures and healing agents are released into fracture surface of matrix to heal the microcrack. Fig. 12b shows the ESEM micrograph of fracture surface of the epoxy composite with 10 wt% PMMA microcapsules after healing performance. The epoxy- and mercaptan-filled microcapsules were homogeneously dispersed in the epoxy matrix. It is clearly observed that the PMMA shell of microcapsules has good interfacial adhesion with epoxy matrix. Also, it seems that PMMA shell of microcapsules has good compatibility with epoxy matrix [4,15]. In Fig. 12b, the fracture surface of composite after healing has a more textured appearance with the incorporation of the healing agent microcapsules. In previous studies, it is suggested that during the fracture occurs more surfaces created in the regions of composite containing microcapsules, which indicates a greater amount

of energy absorption and dissipation before the failure [15].

3.4. Curing reaction studies

The reactivity of self-healing agents can be evaluated by DSC measurements from healing agent mixture and self-healing epoxy composites (Fig. 13). The DSC thermogram in Fig. 13a indicates that even the temperature rise, no reaction occurs in the absence of catalyst in the mixture of epoxy (EC 157) and mercaptan (PETMP). For the mixture of epoxy (EC 157)/mercaptan (PETMP)/BDMA (catalyst) an obvious exothermic reaction peak at 53 °C with onset temperature around 43 °C is detected. It should be noted that the curing reaction between epoxy and its hardener (curing agent) is exothermic in general. In Fig. 13 (c), the flat and smooth curve with increasing temperature shows that the curing behavior of the epoxy matrix with no self-healing agent microcapsules remained almost unchanged [11,33]. The DSC thermograms of the epoxy composites with different contents of healing agent microcapsules at 1:1 (epoxy/mercaptan) weight ratios are presented in Fig. 13(d–g). The epoxy composite samples for DSC measurements were prepared from the crack planes of TDCB samples when the specimens were loaded and tested to failure. All the healing agent microcapsules embedded in epoxy matrix exhibited the similar obvious exothermic peaks centered at about 53 °C due to the exothermic curing reaction between released healing agents (EC 157/PETMP/BDMA) from broken PMMA microcapsules. The increasing of contents of healing agent microcapsules in the epoxy matrix leads to increase the released epoxy and mercaptan/BDMA from broken microcapsules and increase the exothermic peak intensity [15].

4. Conclusions

Microencapsulation of low viscosity epoxy and mercaptan curing agents using PMMA as capsule shell were separately accomplished by internal phase separation method. Chemical and morphological studies of both healing agent microcapsules indicated that PMMA could be used to encapsulation of epoxy and mercaptan without any chemical reactions with core materials. The mean size of epoxy- and mercaptan-filled microcapsules were measured as 21 and 25 μm, respectively. Self-healing epoxy composites were successfully prepared via the incorporation of 2.5–10 wt% of dual-component microcapsules. It was observed that the tensile strength of pure epoxy decreased from 58 MPa to 47 MPa with increasing the concentration of PMMA microcapsules up to 10 wt%. It can be due to the PMMA microcapsules filled with healing agents treat as defects at the cross-section of epoxy composites. The reduction tendency of Young's modulus was also observed for epoxy composites compared to pure epoxy. It can be attributed to the incorporating of thermoplastic PMMA shell in thermoset epoxy matrix and weak interfacial adhesion between PMMA shell and epoxy matrix. The fracture test of virgin and healed TDCB specimens indicated the fracture toughness increases with increase of the concentration of PMMA microcapsules up to 10 wt%. It is suggested that the toughening of epoxy composites is due to crack pinning around the broken microcapsules and increasing the resistance against the growth of the crack. The healing efficiency of epoxy composites increased with increase in PMMA microcapsules content from 2.5 to 10 wt%. The maximum healing efficiency of 80% has been obtained with the 10 wt% of healing agent microcapsules at room temperature after 24 h. DSC results showed that spontaneously curing reaction between healing agents (epoxy and mercaptan) provides self-healing reaction at room temperature. Hence, the healing agent microcapsules prepared in this work can be potentially used in epoxy-based self-healing composites.

Acknowledgments

The authors would like to thank Malek-ashtar University of Technology (MUT) and University of Groningen (RUG) for the financial support for accomplishment of this research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2018.11.041>.

References

- [1] F. Ahangaran, A. Hassanzadeh, S. Nouri, R. Esmaeely Neisiany, Investigation of thermal and dielectric properties of Fe_3O_4 /high-density polyethylene nanocomposites, *J. Compos. Mater.* 51 (28) (2017) 3923–3929.
- [2] M.M. Caruso, D.A. Delafuente, V. Ho, N.R. Sottos, J.S. Moore, S.R. White, Solvent-promoted self-healing epoxy materials, *Macromolecules* 40 (25) (2007) 8830–8832.
- [3] Y.C. Yuan, M.Z. Rong, M.Q. Zhang, J. Chen, G.C. Yang, X.M. Li, Self-healing polymeric materials using epoxy/mercaptan as the healant, *Macromolecules* 41 (14) (2008) 5197–5202.
- [4] F. Ahangaran, A.H. Navarchian, M. Hayaty, K. Esmailpour, Effect of mixing mode and emulsifying agents on micro/nanoencapsulation of low viscosity self-healing agents in polymethyl methacrylate shell, *Smart Mater. Struct.* 25 (9) (2016) 095035 14.
- [5] H. Li, Y. Cui, H. Wang, Y. Zhu, B. Wang, Preparation and application of polysulfone microcapsules containing tung oil in self-healing and self-lubricating epoxy coating, *Colloids Surf., A* 518 (2017) 181–187.
- [6] G. Huyang, A.E. Debertin, J. Sun, Design and development of self-healing dental composites, *Mater. Des.* 94 (2016) 295–302.
- [7] M.M. Escobar, S. Vago, A. Vázquez, Self-healing mortars based on hollow glass tubes and epoxy-amine systems, *Composer B* 55 (2013) 203–207.
- [8] R.S. Trask, G.J. Williams, I.P. Bond, Bioinspired self-healing of advanced composite structures using hollow glass fibers, *J. R. Soc. Interface* 4 (13) (2007) 363–371.
- [9] K.S. Toohey, N.R. Sottos, J.A. Lewis, J.S. Moore, S.R. White, Self-healing materials with microvascular networks, *Nat. Mater.* 6 (8) (2007) 581–585.
- [10] G. Williams, R. Trask, I. Bond, A self-healing carbon fiber reinforced polymer for aerospace applications, *Composer A* 38 (6) (2007) 1525–1532.
- [11] Y.C. Yuan, M.Z. Rong, M.Q. Zhang, Preparation and characterization of micro-encapsulated polythiol, *Polymer* 49 (10) (2008) 2531–2541.
- [12] E.N. Brown, M.R. Kessler, N.R. Sottos, S.R. White, In situ poly (urea-formaldehyde) microencapsulation of dicyclopentadiene, *J. Microencapsul.* 20 (6) (2003) 719–730.
- [13] Y.C. Yuan, X.J. Ye, M.Z. Rong, M.Q. Zhang, G.C. Yang, J.Q. Zhao, Self-healing epoxy composite with heat-resistant healant, *ACS Appl. Mater. Interfaces* 3 (11) (2011) 4487–4495.
- [14] C.L. Mangun, A.C. Mader, N.R. Sottos, S.R. White, Self-healing of a high temperature cured epoxy using poly (dimethylsiloxane) chemistry, *Polymer* 51 (18) (2010) 4063–4068.
- [15] Q. Li, N.H. Kim, D. Hui, J.H. Lee, Effects of dual component microcapsules of resin and curing agent on the self-healing efficiency of epoxy, *Composer B* 55 (2013) 79–85.
- [16] Q. Li, A.K. Mishra, N.H. Kim, T. Kuila, K. Lau, J.H. Lee, Effects of processing conditions of poly(methylmethacrylate) encapsulated liquid curing agent on the properties of self-healing composites, *Composer B* 49 (2013) 6–15.
- [17] F. Ahangaran, M. Hayaty, A.H. Navarchian, Morphological study of polymethyl methacrylate microcapsules filled with self-healing agents, *Appl. Surf. Sci.* 399 (2017) 721–731.
- [18] F. Ahangaran, M. Hayaty, A.H. Navarchian, F. Picchioni, Micromechanical assessment of PMMA microcapsules containing epoxy and mercaptan as self-healing agents, *Polym. Test.* 64 (2017) 330–336.
- [19] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, Autonomic healing of polymer composites, *Nature* 409 (6822) (2001) 794–797.
- [20] T. Theophile, *Infrared Spectroscopy—materials Science Engineering and Technology*, (2012) Shanghai: InTech.
- [21] G. Duan, C. Zhang, A. Li, X. Yang, L. Lu, X. Wang, Preparation and characterization of mesoporous zirconia made by using a poly (methyl methacrylate) template, *Nanoscale Res. Lett.* 3 (3) (2008) 118–122.
- [22] N. Muramatsu, K. Shiga, T. Kondo, Preparation of polyamide microcapsules having narrow size distributions, *J. Microencapsul.* 11 (2) (1992) 171–178.
- [23] H. Guo, X. Zhao, Preparation of microcapsules with narrow-size distribution by complex coacervation: effect of sodium dodecyl sulphate concentration and agitation rate, *J. Microencapsul.* 25 (4) (2008) 221–227.
- [24] A.R. Bachtis, C.J. Boutris, C. Kiparissides, Production of oil-containing crosslinked poly(vinyl alcohol) microcapsules by phase separation: effect of process parameters on the capsule size distribution, *J. Appl. Polym. Sci.* 60 (1996) 9–20.
- [25] H. Zhang, P. Wang, J. Yang, Self-healing epoxy via epoxy-amine chemistry in dual hollow glass bubbles, *Compos. Sci. Technol.* 94 (2014) 23–29.
- [26] E.N. Brown, N.R. Sottos, S.R. White, Fracture testing of a self-healing polymer composite, *Exp. Mech.* 42 (4) (2002) 372–379.
- [27] H. Zhang, J. Yang, Development of self-healing polymers via amine-epoxy chemistry: II. Systematic evaluation of self-healing performance, *Smart Mater. Struct.* 23 (6) (2014) 065004.
- [28] C.L. Mangun, A.C. Mader, N.R. Sottos, S.R. White, Self-healing of a high temperature cured epoxy using poly (dimethylsiloxane) chemistry, *Polymer* 51 (18) (2010) 4063–4068.
- [29] R.E. Neisiany, J.K.Y. Lee, S.N. Khorasani, S. Ramakrishna, Self-healing and interfacially toughened carbon fibre-epoxy composites based on electrospun core-shell nanofibres, *J. Appl. Polym. Sci.* 134 (31) (2017) 44956.
- [30] P.K. Mallick, L.J. Broutman, Mechanical and fracture behavior of glass bead filled epoxy composites, *Mater. Sci. Eng.* 18 (1) (1975) 63–73.
- [31] E.N. Brown, S.R. White, N.R. Sottos, Microcapsule induced toughening in a self-healing polymer composite, *J. Mater. Sci.* 39 (5) (2004) 1703–1710.
- [32] J.D. Rule, N.R. Sottos, S.R. White, Effect of microcapsule size on the performance of self-healing polymers, *Polymer* 48 (12) (2007) 3520–3529.
- [33] J. Lee, D. Bhattacharyya, M.Q. Zhang, Y.C. Yuan, Fracture behavior of a self-healing microcapsule-loaded epoxy system, *Express Polym. Lett.* 5 (3) (2011) 246–253.