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Self-healing glass fiber/epoxy composites with polypropylene tubes containing self-pressurized epoxy and mercaptan healing agents

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ABSTRACT

To improve flowability of the healing agent released from micropipelines without manual intervention, this work prepared a proof-of-concept self-healing glass fiber/epoxy composite, in which plastic (polypropylene (PP)) tubes were embedded and used as containers of epoxy/mercaptan healing agent and foaming agent. Decomposition of the foaming agent at 70 °C created inflated gas in the sealed PP tubes in advance, which increased the internal pressure. Upon damage of the composite, the pressurized healing fluid burst out covering larger cracked plane and enhanced mixing of the liberated epoxy monomer and hardener. As a result, higher healing efficiency was observed as compared to the case without pressurization. The factors that influence healing performance of the system (e.g., tube spacing, content of the foaming agent, foaming time, etc.) were discussed in detail. The proposed approach is believed to have adequate expansibility and can be applied in other self-healing composites with micropipelines.

1. Introduction

Extrinsic self-healing approaches for polymers based on embedded healing agent have attracted substantial interests [1] because chemical structures of the target materials do not need to be changed, which is different from most of intrinsic self-healing systems [2]. Among the available vessels that hold healing agent, micropipelines [3] are capable of storing/providing larger amount of healing agent and sometimes allow for multiple healing function through connection with external supply as compared to microcapsules [4]. Accordingly, a variety of micropipeline configurations have been proposed, including hollow glass tube [5–9], hollow glass fiber [9–14], hollow carbon fiber [15], hollow polymer tube [16,17], and hollow metallic tube [18]. Moreover, microvascular networks were also created by incorporating pre-made microchannels [19–23] or removing pre-loaded microperforms [24–27] from the composites. They proved to work in different composites in terms of mechanical properties restoration.

It is worth noting that flowability of the released healing agent inside materials upon damage is a key issue no matter which type of micropipelines are applied. It determines whether the healing agent can be delivered to the cracked sites and the envisaged healing reaction can be effectively triggered (for two-component healant system). In fact, capillary effect, the main driving factor of healing fluid in self-healing materials with microcracks, becomes rather weak for fiber composites with open fracture [11–13,28–30]. Moreover, the cracks in fiber composites are rather complicated, which may curve and interconnected. Therefore, improvement of flowability of healing agent becomes a very important issue. Otherwise, overlong healing duration or lower healing efficiency would be observed. In extreme situation, for example, the process of healing may even last 12 months [5]. To solve the problem, assistant measures based on manual intervention, such as evacuation [13], heating [11,28,29], dilution with solvent [13,30] and external pressurization [17,24], were used during healing.

The authors of the present paper suggest a novel method by mixing a foaming agent with the encapsulated healing agent. So long as it takes effect, internal pressure is greatly increased and the healing agent would burst out of the reservoir soon after breakage. This self-pressurized system can improve flowability of the healing agent free of manual intervention. More interestingly, the healing agent filled micropipelines might thus be less dense, favoring maintaining original properties of the composites to a higher extent.

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Hereinafter a proof-of-concept glass fiber/epoxy composite is prepared and verified accordingly, in which polypropylene (PP) tubes respectively filled with epoxy and mercaptan as healing components are incorporated. The healing agent has already shown its ability of crack remending of cured epoxy when it is included in microcapsules [31,32]. The PP tubing is selected as micro-container not only because of easy realization of large-scale production, but also owing to the following potential expansibility and advantages (Fig. 1(a)). (i) Healing chemicals can be easily filled into larger size tubes first, and then the tubes size can be reduced by thermal stretching. This would avoid the difficulty of introducing healing agent into small size tubes, while eventually lead to less deterioration of composites mechanical properties as compared to the larger size tubes. (ii) The healing agent-loaded PP tubes can be converted into compartmented versions [33] by, for example, ultrasonic welding. This would help to realize repeated self-healing. (iii) The PP tubes containing healing agent can be purposely deformed due to their flexible nature, so that they can be knitted together with conventional reinforcing fibers. This may favor fabrication of self-healing structural composite with complicated shapes. (iv) Surface of the PP tubes can be modified by physical or chemical techniques, so that the interfacial interaction in composites could be improved. (v) The chemical inertness of PP ensures that it would not react with the included healing agent.

The current work is the first step of our project concerning self-healing composites based on polymeric micropipelines. The main factors that influence rehabilitation efficiency of the fiber composites with self-pressurized healing system, including tube spacing, content of foaming agent, foaming time, etc., are discussed.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (EPON 828, Shell Chemical Inc.) was employed as the composites matrix. Mixture of tetramethylene pentamine (TEPA, Sinopharm Chemical Reagent Co., Ltd., China) and acrylonitrile (Guangdong Guanghua Sci-Tech Co., Ltd., China) served as hardener of EPON 828. Woven glass fabric (E-glass, EWR400-1000, 4.0 × 4.0 plain weave, 0.4 mm thick, 400 g/m^2, China Fiberglass Co., Ltd., China) was chosen as the reinforcement. Diglycidyl 1,2,3,6-tetrahydrophthalate (DTHP, Tianjin Institute of Synthetic Materials Industry, China) and its hardener (mixture of pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, Fluka Chemie AG) and *N*-benzyl dimethylamine (NBDMA, Shanghai Medical Group Reagent Co., Ltd., China)) composed the healing agent. PP tubes (outer diameter: 250 μm, inner diameter: 200 μm, Paradigm Optics, Inc.) were used to contain the healing agent. 2,2′-Azobis-(2,4-dimethylvaleronitrile) (ABVN, J&K Scientific Ltd.) acted as the foaming agent.

2.2. Composites preparation

PP tubes (Fig. 1(b)) were irradiated by UV light (intensity: 95.3 mW/cm^2) at 50 °C for 4 h for embrittlement and surface polarization, which ensures that the tubes would be preferentially damaged when crack propagates in the composites (refer to Fig. S1 in the Supplementary Information). Afterwards, the polymerizable component of the healing agent (i.e. the hand mixing DTHP (100 parts) and ABVN (3 parts)) and the hardener component (i.e. the hand mixing PETMP (100 parts), ABVN (3 parts) and NBDMA (0.4 parts)) were injected into the UV treated PP tubes by a syringe, respectively. Then, the tube ends were sealed with a Pattex Glue Flex Gel adhesive (Henkel AG). Finally, prepregs of healing agent loaded PP tubes (Fig. 1(c)) were made through impregnation in the mixture of EPON 828 (100 parts) and its hardener (21 parts, consisting of acrylonitrile and TEPA at a molar ratio = 0.7) by hand lay-up. In each prepreg, the tube with epoxy and that with the curing agent were alternately arranged to promote the mixing and reaction of healing agents after release.

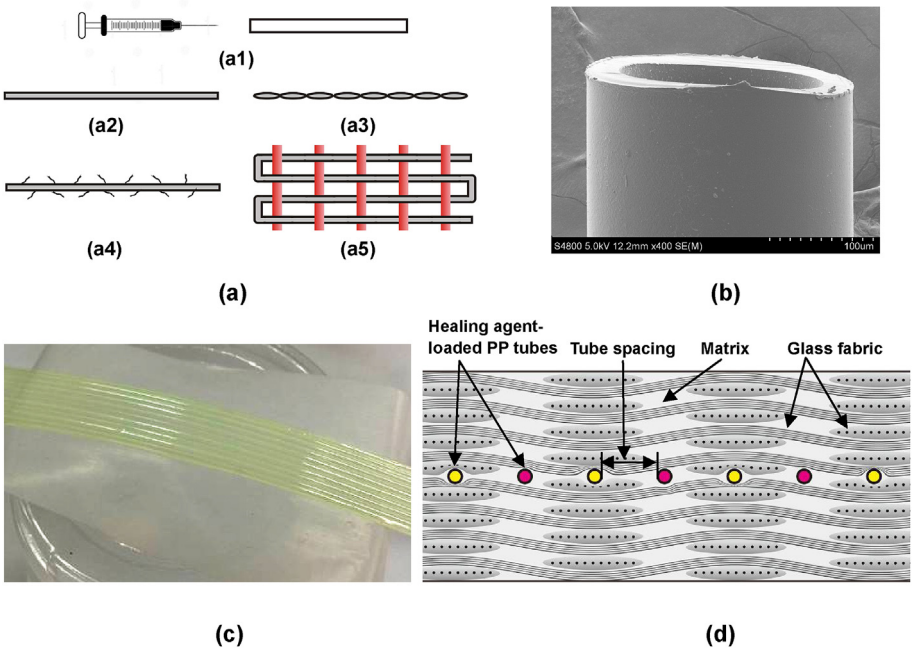

Fig. 1. (a) Expansibility and advantages of thermoplastic tubing in constructing microvascular self-healing composites: (a1) easy incorporation of healing fluid with thicker tubes, (a2) thinning, (a3) compartmented, (a4) surface modification, and (a5) knitted with fiber reinforcement. (b) Scanning electronic microscopy image of a PP tube. (c) Prepreg of healing agent-loaded PP tubes. (d) Arrangement of the healing tubes in the composite laminates. The cross-sections of the tubes containing epoxy and hardener are differently colored to distinguish each other. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To prepare the composite laminates, the woven glass fabric (120 mm × 150 mm) was also impregnated in the above mixture of EPON 828, TEPA and acrylonitrile. Next, eight plies of the glass prepregs with single ply of the PP tube prepreg in the middle (Fig. 1(d)) were degassed for 15 min, compressed to keep the laminates thickness of 2.5 mm, and cured at 25 °C for 24 h and 40 °C for 24 h. Volume fraction of the glass fiber in the composites was estimated to be 41%. To generate higher internal pressure in the PP tubes, the composite laminates were heated to 70 °C for 4 or 8 h allowing gasification of the blowing agent. Model experiments showing the increase of pressure and its effect on outflow of the healing agent due to the activated foaming agent refer to Fig. S2, Table S1 and Fig. S3 in the Supplementary Information. Specimens (120 mm × 25 mm × 2.5 mm) were cut from the laminates along with the longitudinal direction of the PP tubes for further mechanical tests. Each specimen contains 6 vol% healing agent (tube spacing = 750 μm).

The control laminates that do not contain any PP tube prepreg were manufactured under the same condition.

2.3. Characterization

Non-isothermal curing kinetics was studied with a TA DSC Q10 calorimeter in N_2. The heating rates were 2.5, 5, 7.5, 10 and 15 °C/min, respectively. Two measures were conducted for each sample. The curing kinetic parameters were calculated according to Kissinger equation [34].

To assess healability of the system, the composite laminates were damaged by indentation, healed, and evaluated by four-point bend flexural test according to the protocol of Bond and co-workers [13,28,30] as follows. The specimen with back face supported by a steel ring (inner diameter: 20 mm, outer diameter: 35 mm, depth: 10 mm) was indented to the displacement of 1.8 mm by a steel hemispherical end (diameter: 5 mm) at a crosshead speed of 3 mm/min. After indentation, the specimen was allowed to heal the internal cracks at room temperature for a period of time without additional lateral pressure. Four-point bend flexural test was conducted at a crosshead rate of 4.0 mm/min based on ASTM D6272-02. Five specimens were tested for each recipe to get the average value. Healing efficiency was determined by the strength ratio of the healed specimen to the virgin specimen. Typical load-displacement curves of the virgin, damaged and healed laminates containing the PP tubes refer to Fig. S4 in the Supplementary Information. All the mechanical tests were carried out by a WD-5A universal mechanical testing machine. It is noted that the epoxy healing system not only heals the cracks but also provides the composite with higher displacement, which should be ascribed to the higher ductility of the healing material [31].

Scanning electron microscope (S-4800, HITACHI), fluorescence microscope (Axio Oberver Z1, Carl Zeiss) and scanning acoustic microscope (Echo LS, SonixTM, Inc.) were employed to visualize specimens' microstructures. Proceeding of the healing reaction was monitored by in-situ confocal Raman microscope (inVia Raman microscope, Renishaw; excitation wavelength: 875 nm). For this purpose, a 13-μm thick Teflon film was embedded at one end of the composite accompanying the ply of the PP tube prepreg. Having been damaged, the specimen was split along the initial delamination crack and Raman spectra were collected from the fractured surface.

3. Results and discussion

At the beginning, curing kinetics of the epoxy/mercaptan healant with the foaming agent should be known. Accordingly, mixtures of DTHP/ABVN (100 parts/3 parts) and PETMP/ABVN (100 parts/3 parts) were pretreated by heating at 70 °C for 8 h to simulate the foaming process. Afterwards, the pretreated DTHP/ABVN and PETMP/ABVN were quickly mixed with NBDMA (0.4

Table 1
Non-isothermal curing kinetics of the healing agent with and without the foaming agent.[a]

Foaming agent	φ (°C/min)	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	Characteristic parameters
Excluded	2.5	66.1	79.6	93.6	439.4	$\ln A = 5.08$
	5.0	79.6	93.8	105.5	433.0	$E_a = 46.6$ kJ/mol
	7.5	88.1	104.6	122.9	433.8	$n = 0.88$
	10	91.6	109.1	126.0	438.9	
	15	98.3	118.0	141.8	433.0	
Included	2.5	65.7	78.5	87.5	445.4	$\ln A = 4.57$
	5.0	78.9	93.9	106.4	436.2	$E_a = 45.1$ kJ/mol
	7.5	86.7	104.9	124.3	437.1	$n = 0.89$
	10	91.1	109.0	127.3	431.3	
	15	97.5	119.1	144.8	416.9	

[a] φ: heating rate; T_i: onset temperature of the exothermic peak; T_p: peak exothermic temperature; T_f: ending temperature of the exothermic peak; ΔH: heat of reaction; A: pre-exponential factor; E_a: activation energy; n: reaction order.

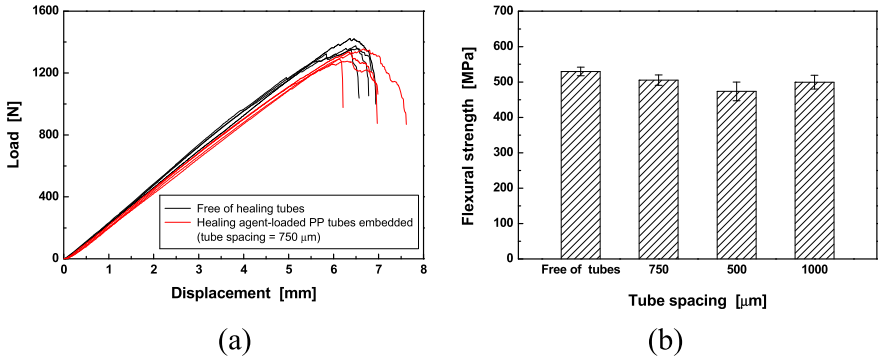

Fig. 2. (a) Load-displacement curves and (b) flexural strengths of the composite laminates with and without the healing agent-loaded PP tubes measured by four-point bend tests.

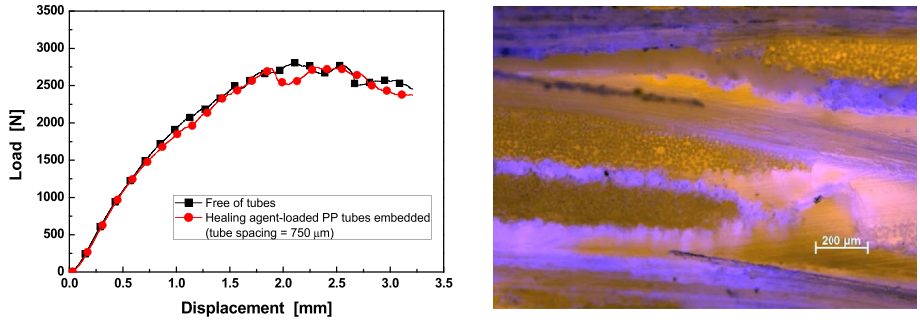

Fig. 3. (a) Typical load-displacement curves recorded during indentation on the composite laminates with and without the healing agent-loaded PP tubes. (b) Fluorescent microscopy photo of cross-section of the composite laminates with the healing agent-loaded PP tubes. The composite was damaged by indentation. To visualize the microstructure, Rhodamine B (0.2 parts) was introduced in the matrix of the specimen, while another fluorescent penetrant, Ardrox 985 (0.2 parts), was added into hardener component of the healing agent. The two chemicals emitted orange and purplish blue glows under illumination of the lights of 525 and 365 nm, respectively. Tube spacing: 750 μm; foaming agent content: 3 parts; foaming condition: 70 °C, 8 h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

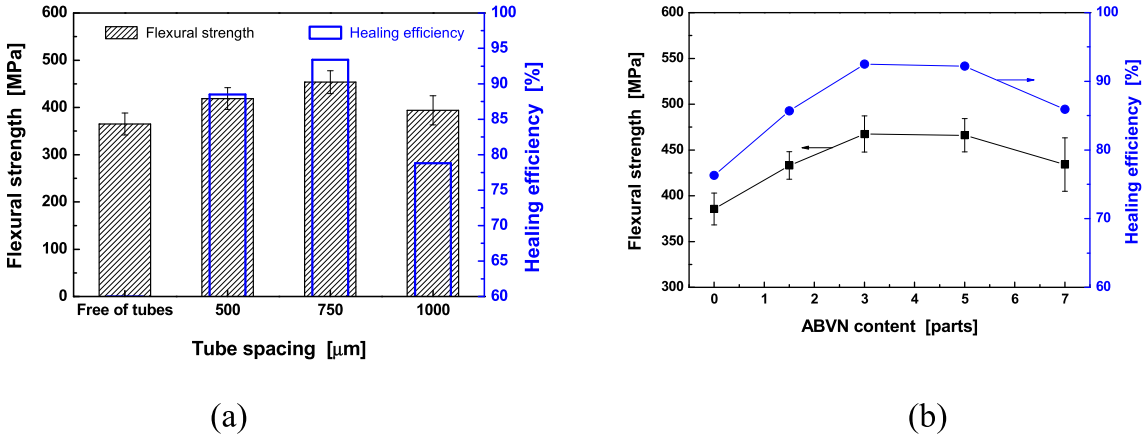

Fig. 4. Effect of (a) tube spacing and (b) foaming agent content on flexural strength and healing efficiency of the damaged and healed composite laminates with the embedded healing agent-loaded PP tubes. Flexural strength of the damaged laminates without PP tubes is shown in (a) as reference. Tube spacing for (b): 750 μm. Foaming agent content: 3 parts; foaming condition: 70 °C, 8 h; healing condition: 25 °C, 7 days.

parts) and then tested by DSC scans under different heating rates (Fig. S5 in the Supplementary Information). For comparison, non-isothermal curing kinetics of the mixture of DTHP (100 parts)/PETMP (100 parts)/NBDMA (0.4 parts) was also measured (Fig. S6 in the Supplementary Information). As listed in Table 1, the systems with and without the foaming agent exhibit similar curing activation energy and reaction order. Evidently, the foaming agent, foaming process and remainder of foaming agent nearly do not affect curing of the healing agent because of absence of chemical interaction between the foaming agent and healant.

On the basis of the above study, we further examine the influence of incorporation of healing agent-loaded PP tubes on mechanical properties of the fiber composites. As non-polar heterogenous substances in the laminates, the tubes would most likely weaken the interfacial interaction, despite the fact that UV pretreatment might somewhat increase surface polarity. It is

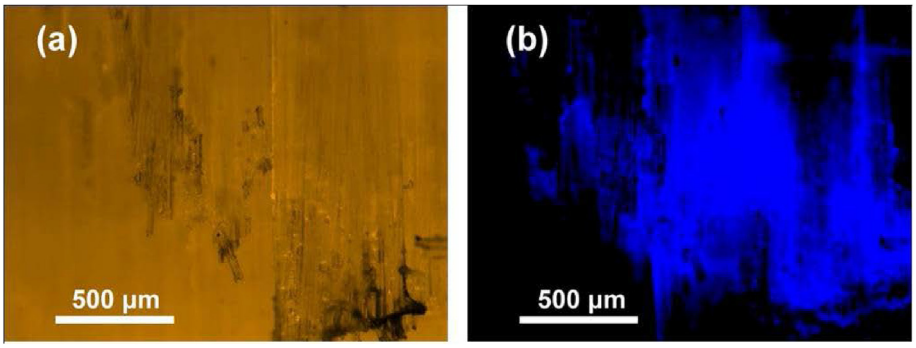

Fig. 5. Fluorescent microscopy photos of back face of the composite laminates with the healing agent-loaded PP tubes (tube spacing: 750 μm; foaming agent content: 3 parts; foaming condition: 70 °C, 8 h). The composite was damaged by indentation. The photos were taken under the lights of (a) 525 nm and (b) 365 nm, respectively. Information of the fluorescent penetrant refers to Fig. 3(b).

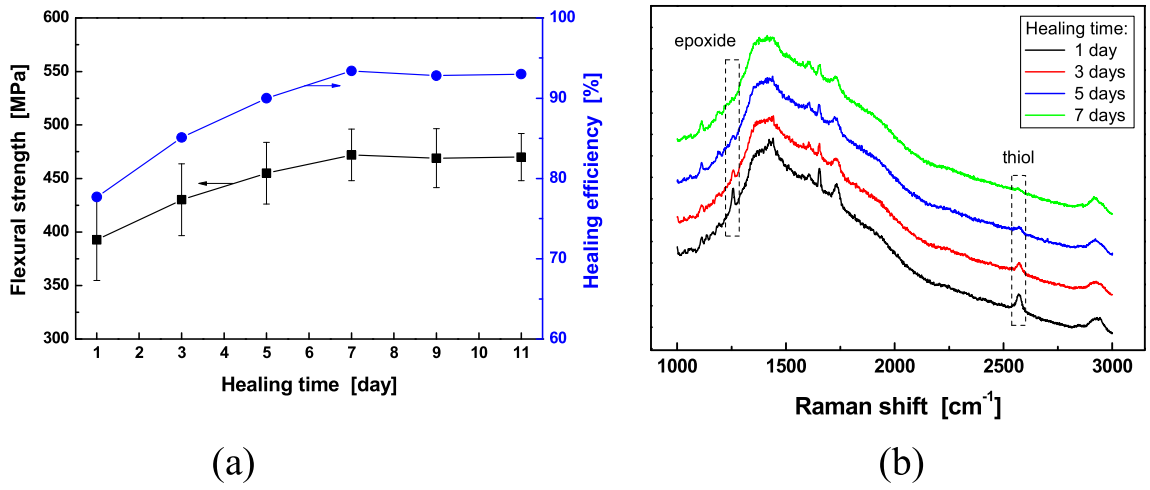

Fig. 6. (a) Effect of healing time on flexural strength and healing efficiency of the healed composite laminates with the embedded healing agent-loaded PP tubes (tube spacing: 750 μm; foaming agent content: 3 parts; foaming condition: 70 °C, 8 h; healing condition: 25 °C). (b) In-situ confocal Raman microscopy spectra collected from the fractured surface of the above composites.

interesting to see from Fig. 2(a) that the composite containing the PP tubes has similar deformation behavior as the one without the tubes. Moreover, flexural strengths of the composites are only slightly reduced after insertion of the tubes (Fig. 2(b)). For example, the highest decrease with a rate of decay of 10.6% is observed in the case of tube spacing of 500 μm. This may be due to the fact that the overall content of the PP tubes is relatively low for the present range of tube spacing of interest, as compared with previous works [11,13,28,30].

According to the data in Fig. 2, the composite with healing agent-loaded PP tubes spaced 750 μm apart is used for the following characterization unless otherwise specified, because it has the greatest retention of strength after all.

As mentioned in the Experimental part, the composite laminates have to be damaged by indentation prior to healing. The load-displacement curves in Fig. 3(a) indicate that with a rise in the indentation depth, the indentation load gradually increases and then decreases. There is no sudden drop of load on the upward slope. It means that delamination and matrix cracking, rather than glass fiber breakage, predominate the failure process at this stage. Although the fracture of PP tubes is not highlighted in this case, it can be reasonably deduced that they must have ruptured together with the surrounding matrix as a result of UV light pretreatment. In this context, the maximum indentation displacement at 1.8 mm is appropriate. Otherwise, a plenty of glass fibers would be broken, which cannot be reconnected by the present healing agent, and the results have to diverge from the theme of this study.

The fluorescent microscopy photo in Fig. 3(b) evidences that the PP tubes have been indeed broken after the indentation. The healing agent was liberated to the cracks in resin-rich region and bundled fibers/matrix interface. The cured version of the healing agent should help to recover the deteriorated mechanical properties of the composite laminates. The deduction is supported by the data exhibited in Fig. 4, which clearly demonstrate that the healing agent must have been bled out so that the damaged specimens containing the healing tubes have higher flexural strength after healing.

A careful survey of Fig. 4(a) reveals that the healing efficiency of the laminates with PP tubes approaches to the maximum at a spacing of 750 μm. The lower value for the tube spacing of 500 μm might result from the harsher damage of the composite under indentation represented by larger amount of broken glass fibers that cannot be reconnected (Fig. S7 in the Supplementary Information). In the meantime, the healing agent released from the tubes spaced 1000 μm might be insufficient for healing, which also leads to poorer healing effect. The competition of these factors yields the highest healing efficiency in the case of tube spacing of 750 μm.

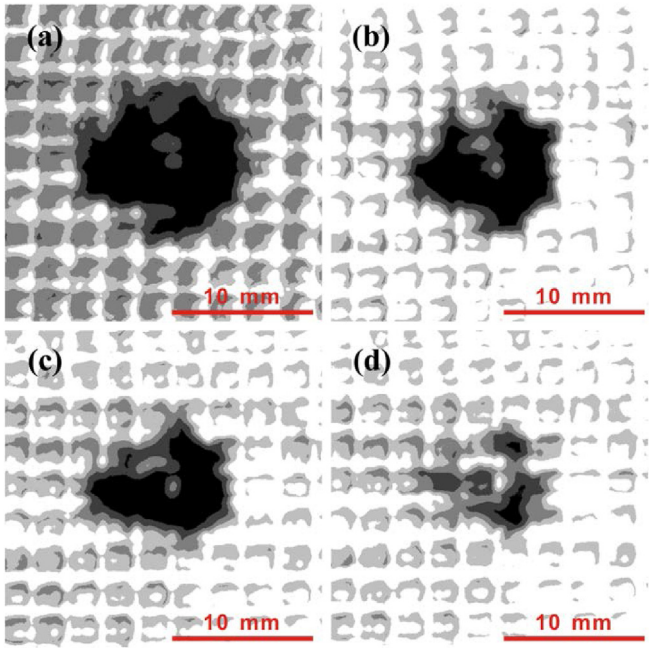

Fig. 7. Ultrasonic T-scan images of the indendation damaged composite laminates with the embedded healing agent-loaded PP tubes (tube spacing: 750 μm; foaming agent content: 3 parts; foaming condition: 70 °C, 8 h; healing temperature: 25 °C). Time of healing: (a) 2.0 h, (b) 12.0 h, (c) 24.0 h, and (d) 36.0 h. Damage area: (a) 74.4 mm^2, (b) 53.8 mm^2, (c) 39.1 mm^2, and (d) 5.4 mm^2.

Since the self-pressurized healing system has proved to work in the composite laminates, the effect of foaming agent (ABVN) concentration, which is directly related to the gas volume created inside the tubes and hence the internal pressure, is investigated (Fig. 4(b)). Initially, the healing efficiency increases with increasing the amount of ABVN. It means that the higher internal pressure has forced diffusion of the healing agent to wider regions. More and more cracked sites are re-bonded. When the AVBN content exceeds

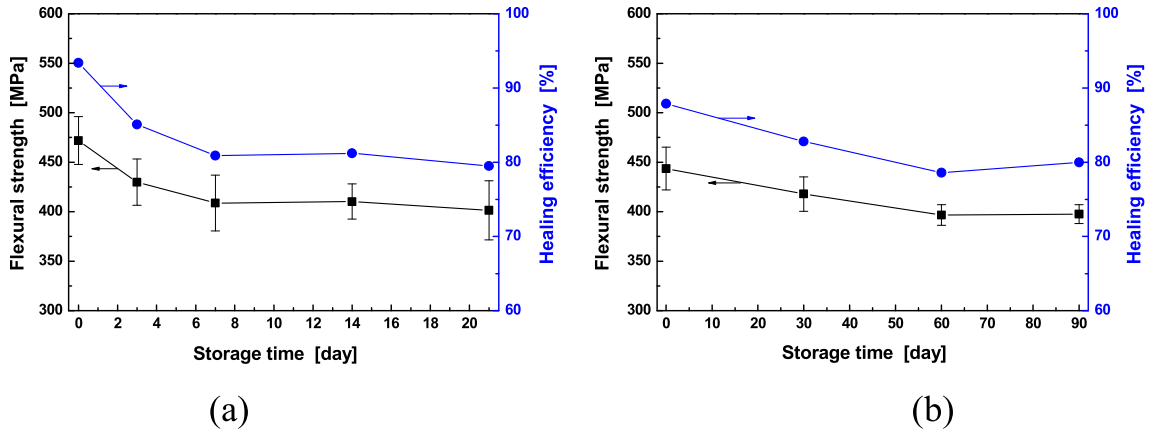

Fig. 8. Effect of room temperature storage time on flexural strength and healing efficiency of the healed composite laminates with the embedded healing agent-loaded PP tubes (foaming agent content: 3 parts). Healing condition: 25 °C, 7 days. Foaming condition: (a) 70 °C, 8 h; (b) 70 °C, 4 h.

3 parts, however, healing efficiency starts to decrease instead of further increasing. It is because the internal pressure was so high to expel quite a few healing agent out of the bulk specimen via the surface damages (Fig. 5), and the amount of the healing agent remaining inside the composites has to be reduced. Besides, the cracks must have interconnected with each other from the middle to the surface of the composite after indentation damaging. With increasing the dosage of the foaming agent, internal pressure in the PP tubes increases, which expells more healing agent out of the composite. Therefore, the dosage of foaming agent or internal pressure should be optimized in favor of maximum utilization of the healing agent.

Fig. 6(a) depicts the dependence of healing efficiency on healing time. It is found that the healing speed is much slower than that of the epoxy composite filled with microencapsulated healing agent (which has the same composition as the present version) [31,32]. The Raman spectra in Fig. 6(b) also show that the epoxide and thiol groups of the released healing agent are almost completely consumed after 7 days, which coincides with the result of mechanical test in Fig. 6(a). In fact, most of the damaged zones have been repaired within 36 h (Fig. 7). Only very small amount of cracks need prolonged healing period. According to these observations, we believe that as soon as the released epoxy monomer and hardener meet on the crack plane, curing reaction takes place, which increases viscosity of the healing agent and hinders movement of the late-comers. Accordingly, the subsequent healing agent can only travel slowly by penetrating the remaining tiny gaps. As a result, the reaction among these unreacted chemicals has to be considerably postponed. For the microencapsulated healing agent, which possesses shorter inter-sphere distance, polymerization of the released healing agent is localized and there is no similar problem.

Lastly, effect of room temperature storage time on the healing capability is evaluated. It is related to the durability of the composites. As shown by Fig. 8, the healing efficiency decreases with the storage time because of gradual leakage of the pressurized gas from the embedded tubes. The depressurization reduces coverage area of the released healing agent and the amount of healed cracks. The analysis is supported by the comparison between Fig. 8(a) and (b). That is, the decline of healing efficiency becomes milder when the foaming time is decreased from 8 h to 4 h. Since shorter foaming time corresponds to fewer decomposition of the foaming agent and lower internal pressure of the tubes, the gas leakage-induced pressure relief is less severe. Accordingly, the healing efficiency plotted in Fig. 8(b) takes much longer time to approach the equilibrium than that in Fig. 8(a). The results reflect a dilemma. Longer foaming time is beneficial for higher healing efficiency but poorer durability. The solution lies in improvement of impermeability of the PP tubes.

4. Conclusions

The present work shows the feasibility of a self-pressurized healing system for self-healing glass fiber/epoxy composites. The core issue lies in the introduction of foaming agent into healing agent-loaded thermoplastic PP tubes. Decomposition of the foaming agent generates gas inside the sealed tubes and pressurizes the included healing fluid. Upon damage of the composites, the released healing agent is driven by the high internal pressure and spreads out over larger cracked planes, as compared with the unpressurized version. As a result, higher healing efficiency is detected.

The factors that influence healing performance of the composites are interconnected. Polymerization speed of the healing agent had better to be lower than its diffusion rate, allowing complete mixing of the components during long-distance delivery [35,36]. This is true, especially in the case of large damages. Additionally, impermeability of the PP tubes should be improved for reducing gas leakage. Although the processing and materials parameters have not yet been optimized, the results of this preliminary exploration have shown that our idea works, which might have broad applicability to other microvascular self-healing composites.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.compscitech.2016.09.020.

References

[1] M.Q. Zhang, M.Z. Rong, Self-healing Polymers and Polymer Composites, Wiley, 2011.
[2] M.Q. Zhang, M.Z. Rong, Intrinsic self-healing of covalent polymers through

bond reconnection towards strength restoration, Polym. Chem. 4 (18) (2013) 4878–4884.
[3] M.-U. Saeed, Z.F. Chen, B.B. Li, Manufacturing strategies for microvascular polymeric composites: a review, Compos. Part A 78 (2015) 327–340.
[4] D.Y. Zhu, M.Z. Rong, M.Q. Zhang, Self-healing polymeric materials based on microencapsulated healing agents: from design to preparation, Prog. Polym. Sci. 49–50 (2015) 175–220.
[5] C. Dry, Procedures developed for self-repair of polymer matrix composite materials, Compos Struct. 35 (3) (1996) 263–269.
[6] M. Motuku, U.K. Vaidya, G.M. Janowski, Parametric studies on self-repairing approaches for resin infused composites subjected to low velocity impact, Smart Mater. Struct. 8 (1999) 623–638.
[7] A. Kousourakis, A.P. Mouritz, The effect of self-healing hollow fibres on the mechanical properties of polymer composites, Smart Mater. Struct. 19 (8) (2010) 085021.
[8] C.J. Norris, J.A.P. White, G. McCombe, P. Chatterjee, I.P. Bond, R.S. Trask, Autonomous stimulus triggered self-healing in smart structural composites, Smart Mater. Struct. 21 (9) (2012) 094027.
[9] H.-B. Yue, J.P. Fernández-Blázquez, D.F. Beneito, J.J. Vilatela, Real time monitoring of click chemistry self-healing in polymer composites, J. Mater Chem. A 2 (11) (2014) 3881–3887.
[10] I.P. Bond, Self-repairing hollow fibre composites, Reinf. Plast. 48 (8) (2004) 16.
[11] R.S. Trask, I.P. Bond, Biomimetic self-healing of advanced composite structures using hollow glass fibres, Smart Mater. Struct. 15 (3) (2006) 704–710.
[12] M. Hucker, I. Bond, A. Foreman, J. Hudd, Optimisation of hollow glass fibres and their composites, Adv. Compos. Lett. 8 (4) (1999) 181–189.
[13] J.W.C. Pang, I.P. Bond, A hollow fiber reinforced polymer composite encompassing self-healing and enhanced damage visibility, Compos. Sci. Technol. 65 (11–12) (2005) 1791–1799.
[14] S. Kling, T. Czigány, Damage detection and self-repair in hollow glass fiber fabric-reinforced epoxy composites via fiber filling, Compos. Sci. Technol. 99 (2014) 82–88.
[15] S. Kling, T. Czigány, Analysis of applicability of the hollow carbon fibres for self-repairing composites, Mater. Sci. Forum 729 (2013) 246–251.
[16] H.R. Williams, R.S. Trask, I.P. Bond, Self-healing composite sandwich structures, Smart Mater. Struct. 16 (4) (2007) 1198–1207.
[17] H.R. Williams, R.S. Trask, I.P. Bond, Self-healing sandwich panels: restoration of compressive strength after impact, Compos. Sci. Technol. 68 (15–16) (2008) 3171–3177.
[18] M. Motuku, U.K. Vaidya, G.M. Janowski, Parametric studies on self-repairing approaches for resin infused composites subjected to low velocity impact, Smart Mater. Struct. 8 (5) (1999) 623–638.
[19] D. Therriault, R.F. Shepherd, S.R. White, J.A. Lewis, Fugitive inks for direct-write assembly of three-dimensional microvascular networks, Adv. Mater. 17 (4) (2005) 395–399.
[20] 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.
[21] C.J. Hansen, S.R. White, N.R. Sottos, J.A. Lewis, Accelerated self-healing via ternary interpenetrating microvascular networks, Adv. Funct. Mater. 21 (22) (2011) 4320–4326.
[22] J.-H. Huang, J. Kim, N. Agrawal, A.P. Sudarsan, J.E. Maxim, A. Jayaraman, V.M. Ugaz, Rapid fabrication of bio-inspired 3D microfluidic vascular networks, Adv. Mater. 21 (35) (2009) 3567–3571.
[23] A.P. Esser-Kahn, P.R. Thakre, H. Dong, J.F. Patrick, V.K. Vlasko-Vlasov, N.R. Sottos, J.S. Moore, S.R. White, Three-dimensional microvascular fiber-reinforced composites, Adv. Mater. 23 (32) (2011) 3654–3658.
[24] A.R. Hamilton, N.R. Sottos, S.R. White, Pressurized vascular systems for self-healing materials, J. R. Soc. Interface 9 (70) (2012) 1020–1028.
[25] A.S. Wu, A.M. Coppola, M.J. Sinnott, T.-W. Chou, E.T. Thostenson, J.-H. Byun, B.-S. Kim, Sensing of damage and healing in three-dimensional braided composites with vascular channels, Compos. Sci. Technol. 72 (13) (2012) 1618–1626.
[26] R.S. Trask, I.P. Bond, Bioinspired engineering study of Plantae vascules for self-healing composite structures, J. R. Soc. Interface 7 (47) (2010) 921–931.
[27] C.-Y. Huang, R.S. Trask, I.P. Bond, Characterization and analysis of carbon fibrereinforced polymer composite laminates with embedded circular vasculature, J. R. Soc. Interface 7 (49) (2010) 1229–1241.
[28] G. Williams, R.S. Trask, I.P. Bond, A self-healing carbon fibre reinforced polymer for aerospace applications, Compos. Part A 38 (6) (2007) 1525–1532.
[29] R.S. Trask, G.J. Williams, I.P. Bond, Bioinspired self-healing of advanced composite structures using hollow glass fibres, J. R. Soc. Interface 4 (13) (2007) 363–371.
[30] J.W.C. Pang, I.P. Bond, 'Bleeding composites'-damage detection and self-repair using a biomimetic approach, Compos. Part A 36 (2) (2005) 183–188.
[31] 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.
[32] 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.
[33] M. Prajer, X. Wu, S.J. Garcia, S. van der Zwaag, Direct and indirect observation of multiple local healing events in successively loaded fibre reinforced polymer model composites using healing agent-filled compartmented fibres, Compos. Sci. Technol. 106 (2015) 127–133.
[34] H.E. Kissinger, Reaction kinetics in differential thermal analysis, Anal. Chem. 29 (1957) 1702–1706.
[35] X.J. Ye, J.L. Zhang, Y. Zhu, M.Z. Rong, M.Q. Zhang, Y.X. Song, H.X. Zhang, Ultrafast self-healing of polymer toward strength restoration, ACS Appl. Mater. Interfaces 6 (5) (2014) 3661–3670.
[36] X.J. Ye, Y.X. Song, Y. Zhu, G.C. Yang, M.Z. Rong, M.Q. Zhang, Self-healing epoxy with ultrafast and heat-resistant healing system processable at elevated temperature, Compos. Sci. Technol. 104 (2014) 40–46.