Development of Composites with a Self-Healing Function

Andrey ANISKEVICH, Sergejs VIDINEJEVS *, Vladimir KULAKOV, Olga STREKALOVA

Institute of Polymer Mechanics, University of Latvia, Aizkraukles 23, LV-1006, Riga, Latvia

crossref http://dx.doi.org/10.5755/j01.ms.21.1.5354

Received 11 September 2013; accepted 02 May 2014

This research aimed to realize experimentally the facile vascular self-healing system in epoxy glass fibre reinforced composite. Using flexible polytetrafluoroethylene tubes as removable preforms, the channels were embedded into both neat epoxy resin and unidirectional glass-fibre reinforced epoxy laminate. Room temperature curable epoxy resin with a surfactant and an amine-based hardener were the components of the binary healing agent. The specimens of tapered double cantilever beam geometry were subjected to Mode I fracture tests. Fracture of specimens released the healing agent from channels and triggered self-healing process of the crack. Tested neat epoxy resin specimens demonstrated recovery of fracture toughness ca. 70 % after 24 h of self-healing at 50 °C. Unidirectional laminate specimens ($250 \times 23 \times 1.2$ mm^3) were made by vacuum infusion method from two layers of glass yarns with 5 embedded channels aligning to reinforcing fibers. The channels were alternately filled with components of the healing agent and then sealed. It was revealed that the embedded vascular channels in specimens had very little effect on their elastic modulus. The experimental program included multiple three-point bending tests of specimens for their initial damage and self-healing of specimens during their heat treatment and following exposure at room temperature. Static and dynamic flexural moduli of elasticity were determined by three-point bending and cantilever beam vibration at all stages of the test program. The healing efficiency was evaluated as a relative change of elastic modulus. The efficiency ca. 30 % was reached during 24 h at 50 °C and additionally increased up ca. 40 % after more than 3 weeks of room temperature exposure. The sealed healing agent was capable of maintaining the capacity for self-healing for at least six months. The research results demonstrated capacity of the macro-channel approach for self-healing realization in multifunctional polymer composite materials.

Keywords: smart composites, epoxy matrix, self-healing, vascular approach.

1. INTRODUCTION

The ability of tailoring the physical and mechanical properties to the requirements of specific technical applications is the intrinsic property of composites, which are produced by combining different constituent materials.

Rapid progress in the development of structural composite materials and their successful implementation into advanced industries (aerospace, shipbuilding and mechanical engineering) have inspired the researchers in the early 1980s to develop a new class of composites, namely smart composites. Smart materials are defined as materials, which possess the ability to change their physical properties in a specific manner in response to a selected specific stimulus in a controlled and predetermined fashion [1]. The actuating stimuli may be various, including environmental factors (pressure, temperature, moisture, etc.), electric and magnetic fields, chemicals, nuclear radiation, etc. Changeable characteristics of smart composites may be associated with variation of their shape, mechanical, optical or electrical properties, viscosity, permeability, and damping. Smart materials include, for example, optical fibres, piezoelectric polymers and ceramics, shape memory alloys, magnetostrictive materials. Owing to their ability to respond to specific stimuli, smart materials find widening applications as various sensors and actuators, i. e. as passive or active materials embedded into the composite structures.

Self-healing or self-repairing materials are one class of smart materials that prompted a great interest of the researchers and actively developed in the last 15 years [2] though the term "self-healing" is older and first time has appeared in 1970 [3].

Only a limited number of polymeric materials, for example hard elastic polypropylene, possess the ability to autonomously self-heal in response to damage, while the majority of other materials require human intervention for repairing damage incurred as a result of mechanical loads or environment influence.

It is well-known that many living biological systems actively react to damage by providing an autonomic healing response at the site of their injury. Therefore, the modern engineering challenge is to understand the principal functional aspects of these natural systems and effectively apply them in designing of synthetic structural materials [4].

Self-healing approaches may be classified as an intrinsic healing by reversible bond formation or extrinsic one by means of triggered release of a pre-added healing system. This system can be embedded within fiber-reinforced composite materials via a liquid healing agent (HA) filled vessels in the form of microcapsules [5, 6] or vascular networks [7, 8], including hollow glass tubes/fibres [9 – 11].

Despite the large number of ideas put forward in respect of self-healing approaches and chemical formulations of a HA including two component chemistry [12], insufficient attention has been paid to creation practically available macro-vascular system for self-healing of a laminated composite. An example could be one-dimensional system of hollow channels embedded into

*Corresponding author. Tel.: +371-29112855; fax.: +371-67820467.
E-mail address: *sergejs.vidinejevs@pmi.lv* (S. Vidinejevs)

a composite material. The channels are filled with a HA of easily accessible chemistry, and serve for HA delivery to a place of damage. Aforementioned chemistry could be polymer resin and appropriate hardener. The components are stored as a binary healing system in separated channels. After rupture, cross-linking of the HA released and rebonding of the cracks are feasible. Thus, the repair of the matrix and restoration of mechanical properties of the composite could be achieved.

The purpose of this study is to test practically the possibility of creating self-healing laminated composites on the base of macro-vascular system and evaluate their self-healing efficiency.

To achieve this goal it was necessary to:

• Develop an easily implemented procedure of manufacturing unidirectional channels of self-healing with the HA;

• Experimentally verify the healing efficiency of pure binder using this system;

• Evaluate from tests the effectiveness of the recovery of the mechanical properties of damaged glass-fiber laminate as a result of self-healing binder.

2. EPOXY POLYMER SPECIMEN FABRICATION

To receive the evidence that the system of channels with binary HA is functional for matrix self-repairing, the experiments with epoxy resin specimens were carried out. The specimens were fabricated from a room-temperature hardened bisphenol-A-(epichlorhydrin) epoxy resin NM 275A and amine hardener NM 275B (Nils Malmgren AB, Sweden) mixed in a mass proportion 100 : 55 as recommended by the manufacturer. According to the technical data, the epoxy resin and hardener have the following characteristics, respectively: density 1.15 g/cm^3 and 1.0 g/cm^3 at 20 °C; viscosity 2000 mPa·s and 150 mPa·s at 25 °C.

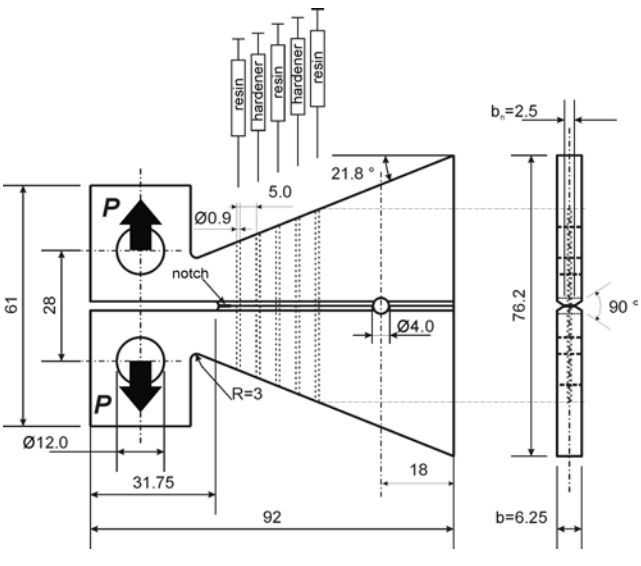


Fig. 1. TDCB specimen with 5 channels filled with binary HA system

A series of tapered double-cantilever beam (TDCB) specimens with geometry shown in Fig. 1 and basically proposed in [13] was poured in a closed silicone rubber mold, where five parallel pretensioned pieces of polytetrafluoroethylene (PTFE) tube of 0.9 mm diameter (TFT20028 Alpha Wire) were placed in a 5 mm distance from each other to preform vascular channels. After the epoxy system curing during 15 hour at 50 °C, PTFE tubes were pulled-out from the TDCB specimens. According to the chart shown in Fig. 1, the hollow channels formed were filled with a binary HA system comprising of epoxy resin NM 275A additionally containing 20 % vol. surfactant 4-nonylphenol (Acros Organics) and hardener NM 275B. After filling, the ends of channels were sealed. For a crack initiation, TDCB specimens were notched with a fine blade. A hole as a crack propagation limiter was drilled through the groove at foundation part of a TDCB specimen (see Fig. 1).

3. TDCB SPECIMENS FRACTURE TESTS

As well-known [13, 14], the main advantages of TDCB Mode I fracture tests are a crack growth along the centerline of specimen and fracture toughness K_{IC} independence of a crack length.

Healing efficiency η was estimated as a ratio of fracture toughness K_{IC} determined for each TDCB specimen in virgin and healed state:

$$\eta = \frac{K_{IC}^{healed}}{K_{IC}^{virgin}} = \frac{P_C^h}{P_C^v}, \quad \text{since} \quad K_{IC} = 2P_C \frac{\sqrt{m}}{\beta}, \qquad (1)$$

where m and β are geometry parameters of a TDCB specimen [13].

A series of 8 virgin TDCB specimens with vascular system filled with the HA was subjected to Mode I fracture tests after manufacture. The tests were carried out on the electro-mechanical testing machine Zwick 2.5 under displacement control, with speed 1 mm/min in three days after HA filling. The imposed load was removed and a test completed when a growing crack reached the limiter. Immediately after the tests, the top entries into the channels were unsealed to ensure a free flowing-out of the HA system inside a cracked region.

Then, unloaded TDCB specimens were kept at 50 °C during 24 h to cure the HA system, which flowed out into the cracked region. View of a self-healed TDCB specimen is shown in Fig. 2.

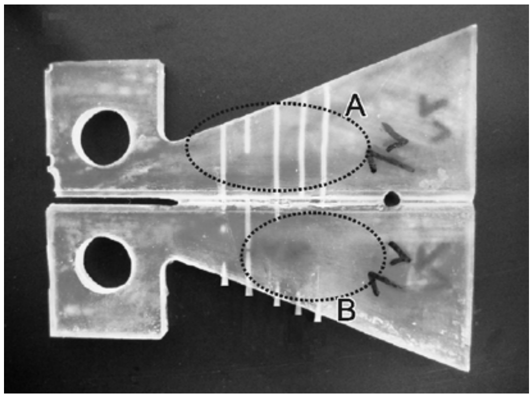


Fig. 2. TDCB specimen after self-healing

It is seen that channels in the upper part A of the specimen are empty since the HA flowed out into the cracked region while the cannels in zone B remain filled.

After the first self-healing procedure, all these specimens were loaded again. Six specimens were subjected to the second self-healing procedure and followed fracture tests. The representative relationship between applied load P and displacement h of the TDCB specimen ends is shown in Fig. 3. Values of fracture loads P_C^v, P_C^h, and P_C^{hh}, corresponding to crack initiation in a virgin, once, and twice healed states of the same specimen, are indicated in the ordinate.

Experimental results obtained in fracture tests, including healing efficiencies η^h and η^{hh} of the specimens once and twice healed correspondingly, are summarized in Table 1.

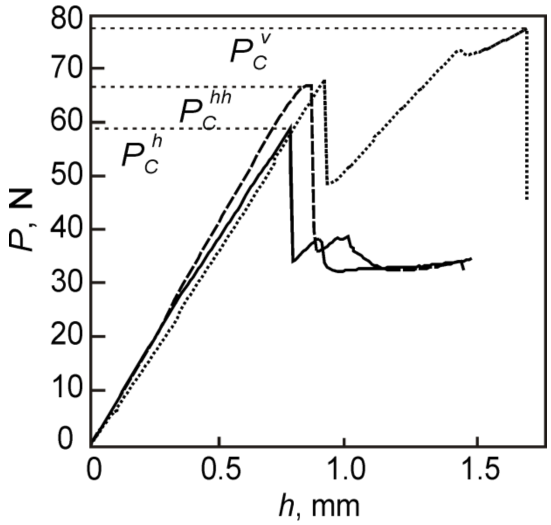


Fig. 3. Representative load vs. displacement curves of a TDCB specimen No. 7. Virgin (dotted line), once healed (solid line), twice healed (dashed line)

A series of 18 TDCB specimens without vascular channels was also fabricated and tested in order to determine initial fracture toughness of a TDCB specimen. Fracture tests gave average value of K_{IC} = 1.20 ±0.23 MPa·m$^{1/2}$, which practically coincides with the value obtained for 8 virgin specimens with vascular channels, filled with HA (see Table 1).

This fact proves that system of vascular channels embedded into TDCB specimen does not degrade its fracture toughness.

The revealed high dispersion of the healing efficiency reflects the objective property of the studied system consequent from additivity of dispersions of different stochastic processes: 1) fracture of specimen and 2) mixture of released binary HA and subsequent cross-linking during fracture rebonding. Thus variance increases from η^h to η^{hh} due to re-fracture and second self-healing (Table 1). The second stochastic process has important features. Firstly, mixing of the HA components (epoxy resin and hardener) along the whole length of cracked region has accidental character that would not provide the required stoichiometric ratio (100 : 55). As a result, HA does not get a degree of cross-linking in the space of crack as a native epoxy. The fracture load of healed specimen is less than that of virgin one. Secondly, the healed substance released in surplus quantity and toughly cured could veer the propagating crack from the centre-line of the groove. Thus, the fracture load of healed specimen could become more than that of virgin one. The assumption used in Eq. (1) about identity of geometry of the groove in virgin and healed state could become crude. Since that, we observed apparent increase in self-healing efficiency sometimes more than 100 %, as well as in [15, 16].

Table 1. Experimental data of TDCB specimens

No	K_{IC}^{virgin}, MPa·m$^{1/2}$	P_C^v, N	P_C^h, N	η^h, %	P_C^{hh}, N	η^{hh}, %
1	1.08	54.6	40.3	74	22.2	41
2	1.07	68.4	34.8	51	55.5	81
3	0.82	43.1	41.0	95	70.3	163
4	1.29	75.0	42.7	57	54.6	73
5	1.54	80.4	44.9	56	–	–
6	1.07	65.7	58.0	88	71.6	109
7	1.31	78.5	60.1	77	72.4	92
8	1.31	72.9	37.4	51	–	–
Mean	1.18 ±0.17			69 ±15		93 ±29

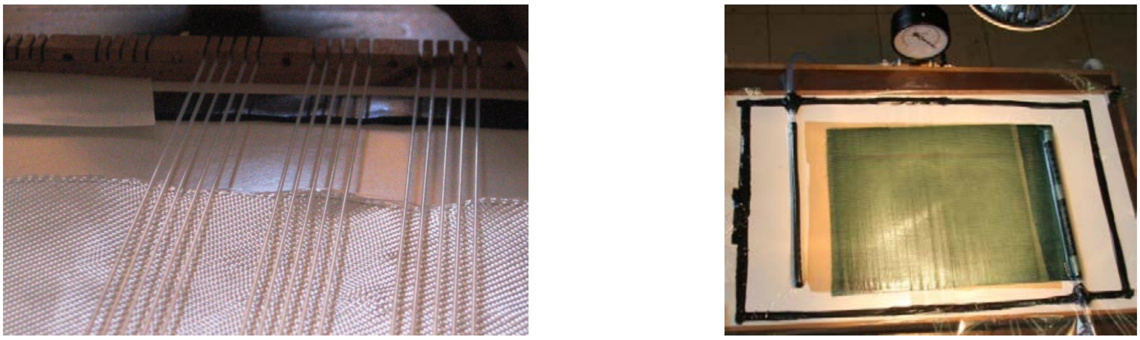
Despite of the above-mentioned difficulties in conducting these fracture tests, it could be resumed that proposed vascular system operates properly and enables to provide a fairly high degree self-healing of TDCB specimens.

4. FABRICATION OF LAMINATE SPECIMENS AND THEIR FLEXURE TESTS

The procedure proven for creating a self-healing system for epoxy resin was applied for fabrication of the vascular channels filled with the binary HA in composite plates (Fig. 4). Three series of plates ($250 \times 300 \times 1.2$ mm^3) A, B and C were manufactured by vacuum assisted resin transfer molding. The plate preforms were manually stacked from two aligned layers of unidirectional fiberglass yarns (500 g/m^2). Two restrictive outer layers of plain glass fabric (AEROGLASS, 110 g/m^2) were stacked on the top and the bottom of the yarns. Room temperature curable epoxy resin LH289 with hardener H289 (with stoichiometric ratio 100 : 33) was used as a binder (Havel Composites s.r.o). Plates of series A were made without vascular channels. To get plates of series B and C with channels aligned to reinforcement, the aforementioned PTFE tubes were embedded into the stacks between the unidirectional fiberglass yarns.

Specimens of $250 \times 23 \times 1.2$ mm^3 size were cut from these plates for three-point flexure tests. Specimens cut from the B- and C-plates have five vascular channels spaced at 4 mm from each other. Epoxy resin NM 275A with additive of 20 % vol. surfactant 4-nonylphenol and hardener NM 275B were used again as a HA system. This type of epoxy has resin/hardener stoichiometric ratio of 100 : 55 close to expected ratio of one of the parts of released HA in the space between two adjacent channels when self-healing has been triggered.

Channels in the B-specimens were filled up only with epoxy resin, while both components of HA system were used in the C-specimens (resin in 1, 3 and 5 channels and hardener in 2 and 4 channels). After filling, all channels were sealed with epoxy mastic. C-specimens were kept at



a b

Fig. 4. Views of manual stacking of a plate perform with PTFE tubes (a) and VARTM process of plate manufacture (b)

the laboratory conditions during 1 – 3 weeks, 2 – 3 months, and 5 – 6 months.

Experimental program of the investigation includes five principal steps, which are shown in Fig. 5.

At step 1, all specimens of the series A, B, and C were tested according to the three-point flexure loading scheme on universal testing machine Zwick 2.5 at constant crosshead rate of 1.2 mm/min and span $l = 100$ mm to determine values of the apparent static flexural modulus in virgin state:

$$E^f = \frac{Pl^3}{4bh^3 w_{\max}}, \qquad (2)$$

where b and h are width and thickness of flat specimen; l is span between the supports; P is applied force; $w_{\max}$ is specimen deflection at the center.

This characteristic is suitable for estimation of mechanical integrity of composite material.

At step 2, all samples were subjected to the procedure of mechanical damage tailored to rupture the specimen matrix and the channels. Multiple damages in the specimens were made by three-point flexure loading with a short span of 20 mm, which were performed ca. every 12 mm along the specimen length. In each bending test, loading continued up to the ultimate stress and completed, when applied load reduced by ca. 30 % of maximum value in the load-displacement curve. Visual assessment verified the multiple breakages of the vascular channels and HA release in filled specimens.

After this damage procedure, in step 3, specimens were subjected to the three-point bending with long span of 100 mm to determine the flexural modulus $E^f_{damaged}$.

At step 4, all damaged specimens were subjected to a heat treatment (24 h at 50 °C) to heal them. Then, in step 5, three-point bending tests with span of 100 mm were used to determine flexural modulus E^f_{healed} after the self-healing. After these tests, specimens were exposed more than 3 weeks at 20 °C and repeatedly tested in three-point bending with span of 100 mm (step 5).

Efficiency of self-healing η was estimated as a ratio of changes of the flexural modulus [12]:

$$\eta = \frac{E^f_{healed} - E^f_{damaged}}{E^f_{virgin} - E^f_{damaged}}. \qquad (3)$$

The experimental data processed are summarized in Table 2. The results obtained in the three-point bending tests are presented in the numerators of this table.

There was awareness in the research that values of P and $w_{\max}$ directly determined in tests are dependent on mutual arrangement of a load/support point position and local damages of a specimen. Thus, such integral characteristics as the apparent flexural modulus calculated using Eq. (2) and healing efficiency estimated by Eq. (3) could become dependent on distribution of local damages in a specimen. To confirm the validity of using the apparent flexural modulus for evaluation of healing efficiency for lengthwise inhomogeneous specimens, another experimental method was applied. Dynamic modulus of elasticity for virgin and healed specimens was determined by method of cantilever beam vibration [17]:

$$E = \frac{12m}{bh^3 L}(2\pi f)^2 \left(\frac{l^2}{3.515625}\right)^2, \qquad (4)$$

where m is mass of specimen; b and h are width and thickness of flat specimen; L and l are total and unclamped length of specimen; f is a frequency of the first natural mode of vibration.

Values of η calculated by Eq. (3, 4) using data of cantilever beam vibration tests for heat treated specimens are presented in the denominators of Table 2.

Firstly, the results obtained indicate that creation of the vascular channels and their fill-up with resin or HA does not practically change modulus E_{virgin} in comparison with the reference specimens of series A. Thus elastic modulus determined in static tests is (24.4 ±0.6) GPa for specimens without channels and (25.2 ±2.0) GPa for specimens with HA in channels (Table 2) are sufficiently close. The values of elastic moduli obtained by both methods are close for lengthwise homogeneous specimens. The apparent static flexural and dynamic moduli of damaged and healed (lengthwise inhomogeneous) specimens more differed and have high dispersion. The objective causes of the scatter of self-healing efficiency are the similar to that of self-healing TDCB specimens.

Additional cause is irreproducibility of the total sample damage via the multiple discrete acts of damage affecting randomly not only the matrix of composite, but often reinforcing fibers in the specimens. In the experiment, it causes a high variation of the starting conditions before the self-healing for the different samples. The results more reflect achievable recovery of specimens in self-healing conditions close to the real performance and warn of high healing efficiency scatter, in comparison with

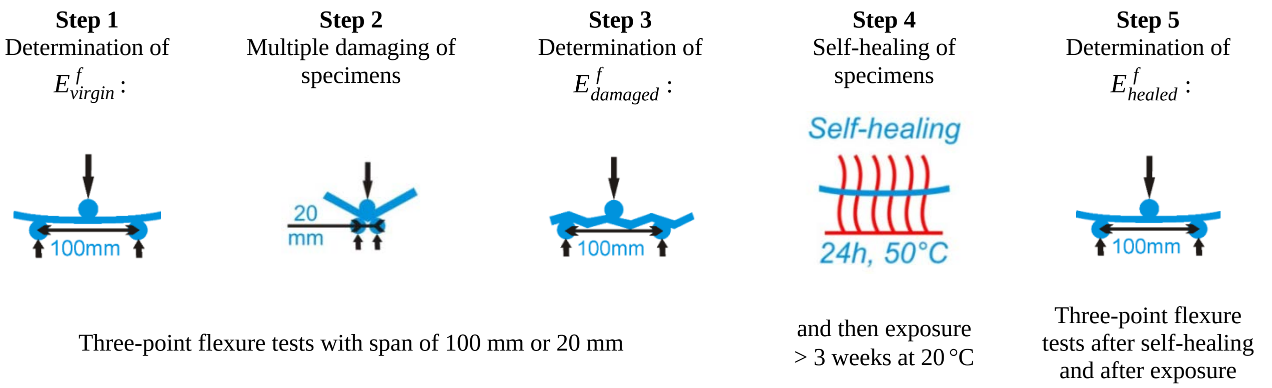


Fig. 5. Stages of experimental program

Table 2. Elastic modulus and healing efficiency of flat specimens determined in static (numerators) and dynamic (denominators) flexural tests

Specimen series		N	E_{virgin}, GPa	η, %	
				24 h, 50 °C*	3 weeks or more, 20 °C**
A	Without channels	9	24.4 ± 0.6 / 21.7 ± 0.8	9 ± 7 / 3 ± 8	10 ± 4 / –
B	Resin in channels	3	25.5 ± 1.6 / 26.4 ± 1.3	14 ± 7 / 13 ± 11	15 ± 5 / –
C	HA in channels1-3 weeks***	13	25.2 ± 2.0 / 23.3 ± 2.0	36 ± 6 / 50 ± 12	52 ± 7 / –
	HA in channels 2-3 months	12		22 ± 6 / 29 ± 9	26 ± 7 / –
	HA in channels 5-6 months	6		26 ± 6 / 35 ± 8	32 ± 10 / –

* for heat treated specimens; ** for specimens after prolonged room exposure; *** exposure before damage; N is number of tested specimens.

the results of other more sophisticated and model experiments. Nevertheless, both estimations of the self-healing efficiency obtained using three-point bending and cantilever beam vibration methods are in good agreement in principle. Thus, static as well as dynamic flexural moduli of flat specimens may be successfully applied for qualitative and quantitative estimation of the healing efficiency.

The main conclusions about healing efficiency are based on comparison between the results of samplings with volume from 9 to 13 trials (specimen series A and C). These samplings provide in fact information about the order of estimated values and their variances. Experimental results reveal that reference A- and B-specimens do not recover their integrity. A small increase of $\eta > 0$ (flexural tests) for heat treated specimens and then constancy of this value at the prolonged room exposure (see Table 2) can be explained by polymerization peculiarities of room-temperature curing epoxy binders used in this investigation. An exothermic nature of polymerization of these binders, reduces the composition gel time, and causes its uneven curing and incomplete conversion of the epoxy groups [18]. Therefore, the additional heat treatment, which caused a greater degree of conversion of the epoxy groups in layered composite, has led to the observed increase of its elastic modulus and healing efficiency.

The experimental results testify that C-specimens with vascular channels filled with HA can be self-healed with a sufficiently high healing efficiency reached up to 36 % in static and 50 % in dynamic flexural tests for heat treated specimens.

Moreover, it is seen that C-specimens retained the high enough ability to self-healing at least six months after manufacturing. The efficiency reached 26 % and 35 % in the mentioned already tests.

It should be noted that self-healing of the composite is time dependent process. The efficiency η increased during the subsequent long-term self-healing exposure of the samples at room temperature. Thus, the efficiency increased from ca. 36 % to 52 % in flexural tests.

A small increase of flexural modulus of A- and B-specimens during their exposure after damage result in corresponding $\eta > 0$ (see Table 2) can be explained by polymerization peculiarities of epoxy binder with cold temperature cure used in this investigation. A large exothermic effect associated with these binders, reduces the composition gel time, and causes its uneven curing and incomplete conversion of the epoxy groups [18]. Therefore, the additional heat treatment, which caused a greater degree of conversion of the epoxy groups in layered composite, has led to the observed increase of its elastic modulus.

5. CONCLUSIONS

This work presents an experimental realization of the concept of a composite with self-healing function. The scientific novelty consists in following.

1) The simple method of making macro-vascular system in the material using flexible PTFE tubes as easy removable preforms was proposed and tested for the embedment of channels into the neat epoxy resin and laminated composite.

2) Two independent systems of channels filled in with epoxy resin and hardener separately were proposed and applied for the storage of HA. The components of HA arbitrary mixed together after release from channels in the place of damage.

Fractured TDCB epoxy specimens demonstrated the healing efficiency (the ratio of fracture toughness of healed and virgin specimen) ca. 70 %.

In laminated specimens, the binary system of self-healing channels proved afford a partial recovering of the composite integrity after sequential procedure of flexural damage. The healing efficiency (the ratio of changes of flexural modulus) ca. 30 % was reached in these specimens after the heat treatment. Self-healing continued during the prolonged exposure at room temperature. Then the efficiency reached ca. 40 %. The sealed HA were capable of maintaining the capacity for self-healing for at least six months.

Thus, the result of the study is the experimental confirmation of the possibility of creating an economical self-healing system based on the macroscopic channels in a laminated composite.

The results obtained can be the basis for the use of the tested technology for different repairing chemistries, as well for the use of existing systems of macro-channels (active cooling, self sensing et al.) in multifunctional polymer composite products for the purposes of self-healing.

Acknowledgments

This work was supported by the ERDF project Nr. 2010/0201/2DP/2.1.1.2.0/10/APIA/VIAA/005.

REFERENCES

1. **Rogers, C. A.** Workshop Summary. Proceedings of U.S. Army Research Office Workshop on Smart Materials, Structures and Mathematical Issues. September 15 – 16, Virginia Polytechnic Institute & State University, Technomic Publishing Co, 1988: pp. 1 – 12.
2. **Guimard, N. K., Oehlenschlaeger, K. K., Zhou, J., Hilf, S., Schmidt, F. G., Barner-Kowollik, C.** Current Trends in the Field of Self-Healing Materials *Macromolecular Chemistry and Physics* 213 (2) 2012: pp. 131 – 143. http://dx.doi.org/10.1002/macp.201100442
3. **Malinskii, Y. M., Prokopenko, V. V., Ivanova, N. A., Kargin, V. A.** Investigation of Self-Healing of Cracks in Polymers. I. Effect of Temperature and Crosslinks on Self-Healing of Cracks in Polyvinyl Acetate *Polymer Mechanics* 2 1970: pp. 240 – 244.
4. **Norris, C. J., Meadway, G. J., O'Sullivan, M. J., Bond, I. P., Trask, R. S.** Self-Healing Fibre Reinforced Composites via a Bioinspired Vasculature *Advanced Functional Materials* 21 (19) 2011: pp. 3624 – 3633.
5. **White, S. R., Sottos, N. R., Geubelle, P. H., Moore, J. S., Kessler, M. R., Sriram, S. R., Brown, E. N., Viswanathan, S.** Autonomic Healing of Polymer Composites *Nature* 409 2001: pp. 794 – 797.
6. **Kessler, M. R.** Self-Healing: a New Paradigm in Materials Design *Proceedings of the Institution of Mechanical Engineers Part G: Journal of Aerospace Engineering* 221 (4) 2007: pp. 479 – 495.
7. **Therriault, D., Shepherd, R. F., White, S. R., Lewis, J. A.** Fugitive Inks for Direct-Write Assembly of Three-Dimensional Microvascular Networks *Advanced Materials* 17 (4) 2005: pp. 395 – 399. http://dx.doi.org/10.1002/adma.200400481
8. **Bejan, A., Lorente, S., Wang, K.-M.** Networks of Channels for Self-Healing Composite Materials *Journal of Applied Physics* 100 (3) 2006: 6 p. article no. 033528.
9. **Dry, C.** Procedures Developed for Self-Repair of Polymer Matrix Composite Materials *Composite Structures* 35 (3) 1996: pp. 263 – 269.
10. **Pang, J. W. C., Bond, I. P.** A Hollow Fibre Reinforced Polymer Composite Encompassing Self-Healing and Enhanced Damage Visibility *Composites Science and Technology* 65 2005: pp. 1791 – 1799.
11. **Trask, R. S., Bond, I. P.** Biomimetic Self-Healing of Advanced Composite Structures Using Hollow Glass Fibres *Smart Materials and Structures* 15 2006: pp. 704 – 710.
12. **Blaiszik, B. J., Kramer, S. L. B., Olugebefola, S. C., Moore, J. S., Sottos, N. R., White, S. R.** Self-Healing Polymers and Composites *Annual Review of Materials Research* 40 2010: pp. 179 – 211. http://dx.doi.org/10.1146/annurev-matsci-070909-104532
13. **Brown, E. N., Sottos, N. R., White, S. R.** Fracture Testing of a Self-Healing Polymer Composite *Experimental Mechanics* 42 (4) 2002: pp. 372 – 379. http://dx.doi.org/10.1007/BF02412141
14. **Brown, E. N.** Use of the Tapered Double-Cantilever Beam Geometry for Fracture Toughness Measurements and Its Application to the Quantification of Self-Healing *Journal of Strain Analysis* 46 2011: pp. 167 – 186.
15. **Keller, M. W., White, S. R., Sottos, N. R.** A Self-Healing Poly(Dimethyl Siloxane) Elastomer *Advanced Functional Materials* 17 2007: pp. 2399 – 2404. http://dx.doi.org/10.1002/adfm.200700086
16. **Yuan, Y. C., Rong, M. Z., Zhang, M. Q., Chen, J., Yang, G. C., Li, X. M.** Self-Healing Polymeric Materials Using Epoxy/Mercaptan as the Healant *Macromolecules* 41 2008: pp. 5197 – 5202.
17. **Hunt, J. F.** Cantilever-Beam Dynamic Modulus for Thin Fiberboard Composite Products. Part 2. Property Comparison with Bending Modulus *Proceedings of the 16th International Symposium on Nondestructive Testing and Evaluation of Wood* Beijing, China, October 12 – 14, 2009: pp. 231 – 241.
18. **Chursova, L. V., Roskutin, A. E., Gurevich, Ya. M., Panina, N. N.** Cold Cure Binder for Construction Industry *Adhesives. Sealants. Technology* 5 2012: pp. 40 – 44 (in Russian).