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Self-healing composite with glass ionomer based microcapsules: Preparation and evaluation of fracture toughness and crack healing efficiency

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***Abstract*---**Background: Limitations of dental composite have dictated the need for development of new self-healing composite. Aim: To evaluate the effect of adding an experimentally prepared glass ionomer-based microcapsule to commercially available flowable composite on its fracture toughness and healing crack efficiency. Methodology: Seventy composite specimens were divided into two groups according to the material used, group C: as-received commercially available flowable composite while group HC: commercially available flowable composite modified by adding experimentally prepared self-healing microcapsule. Preloading of the

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specimens with a fixed load (60 N) was done before the storage period. The fracture toughness (K_{IC}) was measured for each group after three days of water storage. The crack healing efficiency of HC group was also evaluated mechanically, chemically and morphologically. Results: Group HC revealed a statistically significant higher fracture toughness when compared to that of group C after three days of water storage. Moreover, there was significant higher percentage of crack healing efficiency recorded for the HC group (19%±2.53) when compared to that of the control group. Conclusion: Incorporation of 5 wt% self-healing microcapsules containing copolymer of polyacrylic acid and fluoroaluminosilicate into commercially available flowable composite provided a promising improvement in terms of the fracture toughness and crack healing efficiency of commercially available flowable composite after three days of storage.

***Keywords*---**self-healing, dental composites, dental material, encapsulation.

Introduction

Bulk fracture, along with discoloration, of resin composite remain among the most common causes of failure of composite resin restorations (1). Bulk fracture in resin composite is commonly initiated by microcracks. These microcracks are induced by mechanical fatigue in the oral environment. They are hard to detect, and almost impossible to repair manually. If microcracks are left untreated, they may cause deterioration of the restoration, which eventually leads to catastrophic failure (2). Therefore, extensive efforts have been made to significantly improve the composite longevity.

Attempts to improve the resistance to crack initiation and to repair cracks within resin composite include increasing the inorganic filler level and decreasing the filler particle size to the nanoscale. Also, incorporating reinforcing agents such as whiskers and fibers, changing the polymer chemistry as well as altering the polymerization reactions mechanism were reported (2).

A new approach to prevent microcracking and fracture of current dental resin composites is self-healing. Self-healing concept refers to autonomic repair systems that naturally occur in biological systems (2). Self-healing materials are those capable of restoring their mechanical integrity following microcracks formation. Thus, continuous efforts are made to produce materials with self-healing capabilities.

The self-healing resin composite involves embedding microcapsules containing healing liquid into the resin matrix. When microcracks develop in the resin matrix, the microcapsules will rupture by the crack impact to release the healing liquid. The healing liquid then flows into the crack planes, thus exposing itself to the catalyst in the resin. This interaction initiates the self-healing process through polymerization of the healing liquid, filling the crack, and finally bonding the cracked planes together (3).

The first attempts of self-healing composites suffered from several downsides as the potential toxicity of the monomers and the cost of the catalyst. To overcome the previously reported shortcomings, a newer model of self-healing dental composites was developed. These self-healing models were based on using the glass ionomer cements (GICs) as the healing agent (2). This has introduced a new era of intelligent materials which may offer significant enhancement in extending the service life of polymeric materials.

Therefore, the aim of the current study was to prepare and incorporate glass ionomer (GIC)-based microcapsules into commercially available flowable composite. The null hypothesis was that there will be no significant difference in fracture toughness and crack healing efficiency measured after three days water storage between the flowable composite containing self-healing microcapsules and fluoroaluminosilicate particles and the as- received commercially available flowable composite.

Materials & Methods

Sample size calculation was performed using G*Power version 3.1.9.2, FranzeFaul, University Kiel, Germany. Mean and standard deviations were determined according to Wu et al. (2019) (4), based on the fracture toughness test ($MPa.m^{1/2}$). Using alpha level of significance (α) 0.05 and power of the study 0.8, 20 specimens for each group were sufficient to produce an effect size of 1.487.

Seventy specimens were randomly assigned into two groups (35 specimens in each group) according to the type of composite used. The control group (C) was comprised of as-received commercially available flowable composite (NexComp Flow) while the intervention group (HC) was of modified flowable composite by adding strontium fluoroaluminosilicate glass powders and self-healing microcapsules.

Preparation of the Self-healing Composites:
Preparation of the Self-healing Microcapsules

The self-healing microcapsules containing polyacrylic acid known as healing liquid (HL) were prepared using the water-in-oil (W/O) microemulsion method. The steps of preparation according to **Galgali et al.** (2011) (5) are summarized and illustrated in **Figure (1).**

Briefly, a mixture of 4.0 mL span 80 surfactant, 100 mL cyclohexane, 4.0 mL milli-Q water, and 4.0 mL copolymer of polyacrylic acid (HL) were weighed and stirred for one hour at room temperature. Simultaneously, another beaker containing 4 ml of Tetraethyl orthosilicate (TEOS) and 1 m of hydrochloric acid was mixed to prepare silica solution by sol-gel technique **(Figure (1A)).** The silica solution was then added dropwise to the polyacrylic acid solution and stirring continued for 45 minutes at 60 °C **(Figure (1B)).** The resulting precipitate was then collected by filtration technique, leaving a particulate powder (microcapsules containing HL) **Figure (1D-E).**

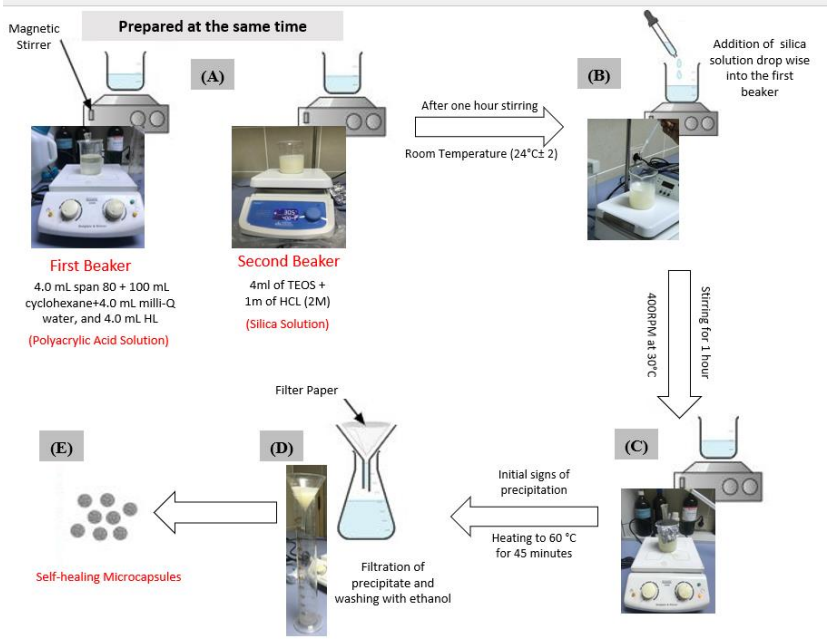

Figure (1). A schematic diagram representing the steps of self-healing microcapsules preparation

Characterization of the Prepared Self-healing Microcapsules

Morphological characterization of the self-healing microcapsules was carried out by SEM (SEM Quanta FEG 250 with field emission gun, FEI Company, Netherlands). The specimens were sputter-coated with gold palladium and then scanned by SEM at various magnifications.

Chemical characterization of the self-healing microcapsules containing healing liquid was carried out by FTIR (IR Spirit-T FTIR, Shimadzu, Kyoto, Japan) immediately after preparation. A microcapsule containing water only was prepared by the same method of self-healing microcapsules previously described and was used as a reference group.

Incorporation of the Prepared Healing Microcapsules into Composite

The prepared self-healing microcapsules were surface treated with a silane coupling agent **(Bis-Silane™)** prior to incorporation in the flowable resin composite. Silanization was done in order to form a strong bond with the composite methacrylate resinous matrix and ensure the fracture of microcapsules in response to crack propagation The self-healing microcapsules were added to 10 ml of silane coupling agent in the bottle, stirred for five minutes at room temperature, and then recollected by filtration technique**.**

The silanized self-healing mirocapsules were then incorporated into a commercially available flowable composite (Nexcomp Flow META BIOMED, Korea) following the technique described by Sharma et al.(6). In such technique, 45 wt%

of NexComp Flow composite, 50 wt% of strontium fluoroaluminosilicate glass powder and 5 wt% silanized self-healing microcapsules were weighed and then mixed using a homogenizer (Ultra-Turrax T Model 18, IKA, Germany) at 3500 RPM for one minute, followed by hand mixing on a glass slab with a spatula. The hand mixing process was repeated until the mixture became a uniformly mixed clay-like substance**.** The mix was then placed in a sealed dark container and stored in an incubator (Binder Tuttlingen, Germany) for 24 hours at room temperature before specimen preparation.

Specimens Preparation

A total number of 40 rectangular single edge notched bar specimens (12 mm length× 3 mm width× 4 mm thickness) were fabricated to measure the fracture toughness according to the ASTM D5045-14. A split metal mold with a razor blade inserted at the midspan of the mold was used to construct the specimens. This blade was used to produce a sharp notch with length/width (a/w) ratio equals 0.5 within specimen**.** (7, 8).

The specimens for both groups were then prepared following the manufacture instructions. The composite was packed in the metal mold with a round stainless steel burnisher. Pressure was applied to extrude any excess composite material. Each specimen was photo-cured using a LED light-curing unit (Elipar S10, 3M, ESPE, USA) which was placed at a distance of 3 mm perpendicular to the surface for 20 seconds on both sides of the assembly**.** After that, any residual material was removed and polished until the surface became smooth**.** The specimens were then stored in the incubator for 24 hours at room temperature (24°C± 2) prior to testing.

Testing Procedure
Fracture Toughness Test

According to Huyang et al. (2016) (2), an initial load of 60 N was applied on the specimens of both groups by means of universal testing machine (Computer controlled Instron model 2519 series, Instron Corp., Canton, MA, USA) with a load cell of 5 kilo Newtons (KN) in three-point flexure at a crosshead speed of 0.5 mm/min. The specimen notch was placed on the tensile side and the loading pin was aligned with the notch. This test was carried out to induce cracks within the specimens that critically fracture them without complete separation. After initial loading of all specimens, they were immersed in distilled water and stored in an incubator at 37 °C prior to performing the final fracture toughness test**.** The fracture loads (N) were recorded and then, fracture toughness was calculated according to ASTM D5045-14 via the following equation: (7, 9, 10).

$$K_{IC} = [3\ P\ L\ a^{1/2} / 2\ b\ w^2] \times f(a/w)$$
$$f(a/w) = [1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.80(a/w)^4]$$

where:
K_{IC}: is the fracture toughness in (MPa.$m^{1/2}$) - **P**: is the load at failure in Newton (N) - **L**: is the distance between the supports in mm (10 mm) - **t**: is the thickness

of the specimens in mm (4 mm) - **a**: is the notch length in mm (1.5 mm) - **w**:is the width of the specimens in mm (3 mm) - **f:** is the function of (a/w) (obtained from ASTM-E399).

The Crack Healing Efficiency

The Crack healing efficiency for healing Composite (HC) group was investigated in the current study mechanically, chemically, and morphologically. The control group was used as a reference group.

Mechanical Evaluation:

Mechanical evaluation was carried out by measuring the fracture toughness after three days of water storage (healing period) and then calculating the percentage of healing efficiency for both groups according to:

$$\%K_{IC} = K_{IC}(\text{healed}) / K_{IC}(\text{initial}) \times 100\% \quad (11)$$

where **($\%K_{IC}$)** represents the percentage of healing efficiency, **K_{IC} (healed)** represents the fracture toughness of healed specimens after three days storage and **K_{IC} (initial)** represents the fracture toughness calculated by initial load (60 N) in which the specimens were critically fractured.

Chemical Evaluation:

Chemical characterization was done by means of FTIR. A total of 15 rectangular specimens for each group (n=15) were prepared as mentioned previously. Each group was scanned twice. One spectrum was obtained immediately after preparation of the specimens. The other spectrum was recorded after initial loading and three days of water storage. Scans were collected from 500 cm^{-1} to 2500 cm^{-1} at 4 cm^{-1} resolutions.

Morphological Evaluation:

A total of 15 rectangular specimens for each group were imaged without coating by using low-voltage mode of SEM operation (0.3–4 kV). The SEM scans at magnification 130x, 250x and 500x were used to detect the surface changes after initial loading and waters storage.

Statistical analysis

Data were explored for normality using Kolmogorov-Smirnov and Shapiro-Wilk tests. Data were reported as mean and standard deviation values in case of parametric distribution. Independent sample t-test was used to compare between two groups in non-related samples while paired t-test was used to compare between two groups in related samples. The significance level was set at $P \leq 0.05$. Statistical analysis was performed with IBM® SPSS® Statistics Version 22 for Windows.

Results

Characterization of the self-healing microcapsules
Morphological Characterization

Scanning electron micrographs of various magnifications revealed the formation of silica microcapsules with average diameter of the microcapsules was 2.15 µm ± 0.31 Figure (2 a-b).

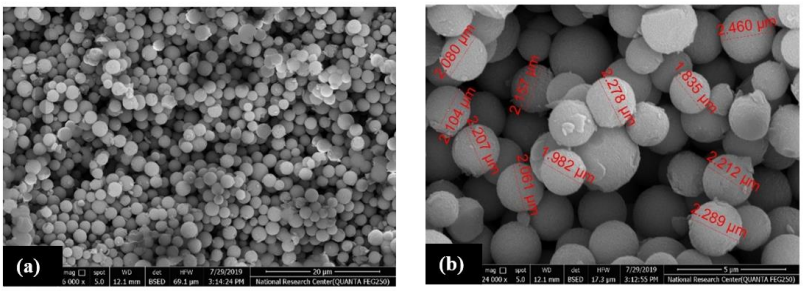

Figure (2). Scanning electron micrographs for self-healing microcapsules a) 1500x magnification b) 24000x magnification with an average diameter 2.15 µm ± 0.31

Chemical Characterization

FTIR spectra of the self-healing microcapsules Figure (3) revealed the presence of –COOH groups with an absorbance peak at 1700 cm^{-1}. However, –COOH group peak was not observed in the preprepared control microcapsules containing water. An absorbance peak at 2400 cm^{-1} (-OH group) was evident in all groups with different intensities; the highest intensity recorded for the microcapsules containing water.

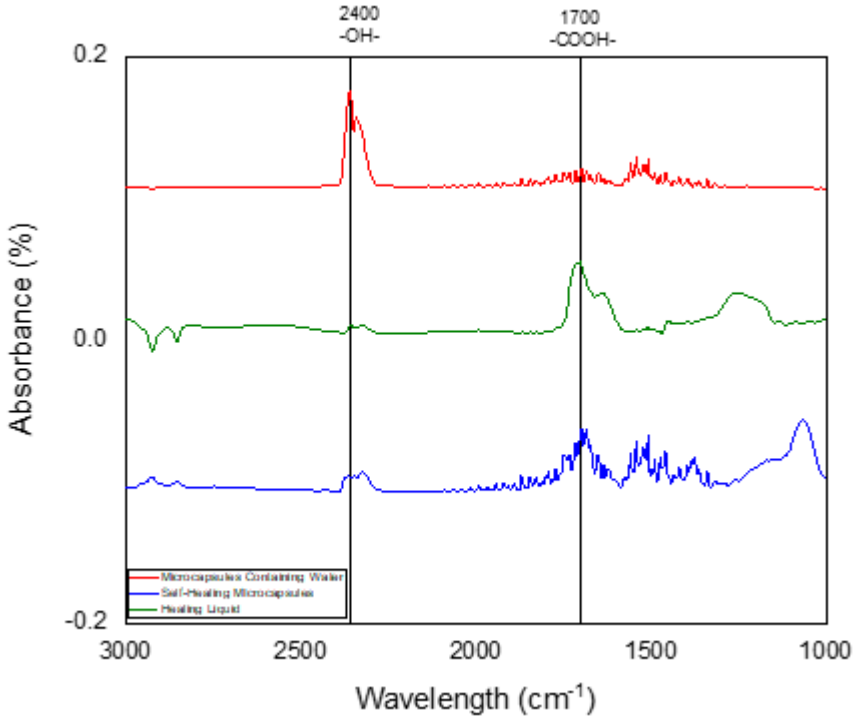

Figure (3). FTIR spectra of the microcapsules containing water, self-healing microcapsules and healing liquid

Results of fracture toughness

The HC group (n=20) revealed a statistically significant higher fracture toughness mean value (0.12 MPa.$m^{1/2}$ ± 0.02) compared to the control group (0.074 MPa.$m^{1/2}$ ±0.01) after three days from initial loading.

Results of the Crack Healing Efficiency

Results of Mechanical Evaluation

The HC group revealed statistically higher percentage of crack healing efficiency of (19% ± 2.53) compared to that of the control group (10% ± 0.98) where p-value was < 0.001**.**

Results of Chemical Evaluation

The FTIR spectra for both groups immediately after specimens' preparation are shown in **Figure (4a).** The chemical analysis of HC group revealed the presence of -COOH group with absorbance peak at 1700 cm^{-1}. Such absorbance peak was not observed in the control group. However, the FTIR spectra of HC group after initial loading and water storage for three days **Figure (4b)** revealed the presence of silicic acid (H_4O_4Si) and Si-O-Al group. Such groups were identified as absorbance peaks at 1050 cm^{-1} and 800 cm^{-1}, respectively. Moreover, absorbance peak at 1700 cm^{-1} (related to -COOH-) was present in the HC group. However, such absorbance peaks were not observed in the control group.

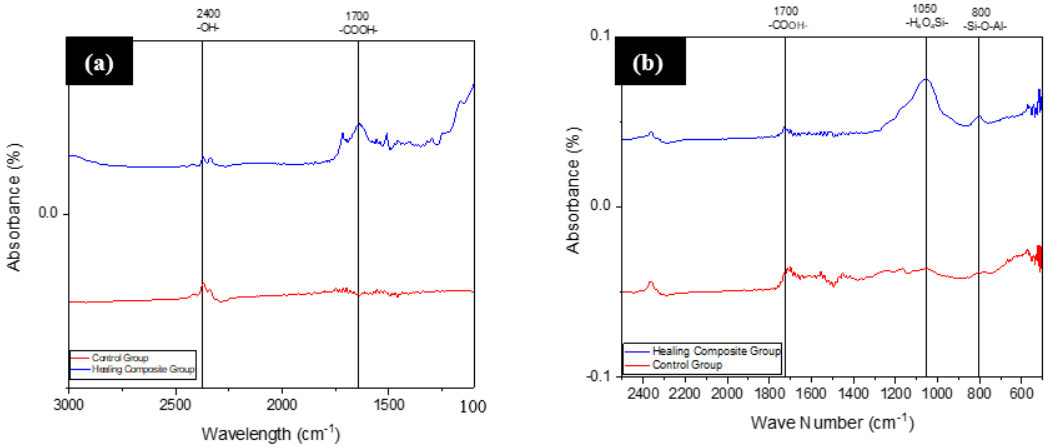

Figure (4). FTIR spectra of both groups (a) immediately after specimens' preparation (b) after three days water storage

Results of Morphological Evaluation

The scanning electron micrographs for HC preloaded specimens after water storage displayed small areas of a material with less density around the prepared notch. Intact self-healing microcapsules which did not fully rupture were also observed (denoted by the red dotted circles) Figure (5a). These observations were not evident in micrographs for control group Figure (5b).

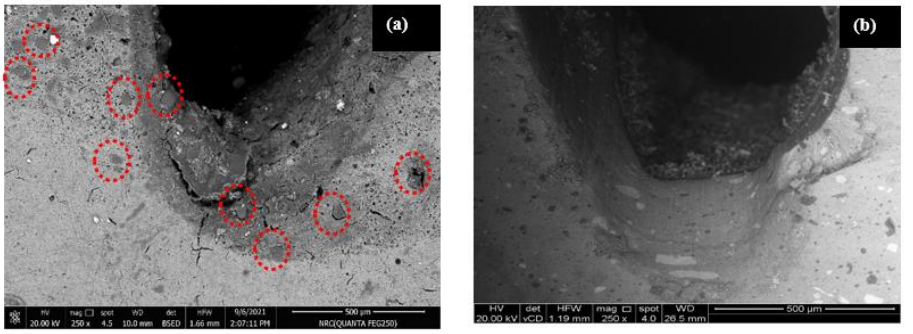

Figure (5). Scanning electron micrographs (250x) of both groups a) HC group after three days (Red dotted circles denote intact microcapsules) b) control group

Discussion

Despite the efforts that have been made to improve the composite properties, composite restorations are still challenged mainly by bulk fracture. Self-healing composite have been introduced to overcome such problem (12, 13). Therefore, the aim of the current study was to reveal the effect of adding "an experimentally

prepared microcapsule containing copolymer of polyacrylic acid as healing liquid" on the fracture toughness and the healing crack efficiency of commercially available flowable composite, compared with unmodified flowable composite.

In the current study, the encapsulation of the copolymer of polyacrylic acid (HL) was achieved by water-in-oil (W/O) microemulsion as the healing agent used was in the aqueous phase as recommended by Huyang et al. (2016).(2). Silica was the material of choice for encapsulation owing to the close matching of its elastic modulus with that of the fillers in the dental composites. This would prevent the premature fracture of the microcapsules during healing composite preparation (14, 15).

The average diameter of microcapsules obtained was in agreement with the findings reported by Zhu et al. (2015) (15) who concluded that the size of the prepared microcapsules depended mainly on the selected encapsulation technique. Such size of microcapsules in the current study is believed to be within the optimal size range. This is because, it was large enough to enclose sufficient healing liquid in contrast to the nanosized capsules without affecting the mechanical performance of the healing composite that was reported with the larger microcapsule's sizes. (16).

FTIR was used to chemically characterize the self-healing microcapsules. The -COOH peak at 1730 cm^{-1} in the microcapsules containing HL confirmed the presence of healing liquid within the silica microcapsules as reported by other studies (2, 17, 18). Silanization of microcapsules was done by 3-methacryloxypropyltrimethoxy silane (MA-silane) coupling agent. (17)

In the current study, the self-healing dental composite was prepared from two clinically commercially available dental restorative materials which are flowable resin composite and GIC. The commercially available composite used in the current study (Nexcomp Flow composite) was chosen due to the presence of the hydrophilic HEMA monomer which would allow the movement of water required for initiating the GIC reaction during the healing process (19). The percentage (5 wt %) of self-healing microcapsules was selected based on Huyang et al. (2016) (2) who reported that such percentage was optimal to obtain healing efficiency without reducing the mechanical properties of the composite.

In the present study, the mechanical evaluation for both groups was carried out by the fracture toughness test. The 3-point bending fracture toughness was the test of choice because it is a good predictor of the clinical performance of composite resin restorations. This is because a direct relationship exists between the clinical failure and the low fracture toughness of the material. (20).

The fracture toughness (K_{IC}) and the healing efficiency of healing composite specimens were measured by the method used in the University of Illinois at Urbana-Champaign (UIUC) models (12, 21). This method involves stressing the sample with a predetermined load (60 N), then initial fracture toughness was calculated**.** After initial loading, both groups were stored in water for three days which was essential to permit the diffusion of the healing liquid from the microcapsules and the formation of GICs.(2)

The increase in K_{IC} (0.12 MPa.$m^{1/2}$) of healing composite (HC) group after healing period may be due to the presence of intact microcapsules which may act as reinforcing agent in the composite. Such intact microcapsules may be attributed to "the capsule-crack interaction" which is affected by the stiffness of microcapsules (22). The results of K_{IC} in the current study were in agreement with the results of Brown et al. (2004) (23) who reported that the fracture toughness of composite loaded with healing microcapsules significantly increased after a healing period of three days when compared to that of neat composite. However, the value of K_{IC} recorded by Huyang et al. (2016) (2) for the healing composite after four days was 0.22 MPa.$m^{1/2}$ which appeared to be higher than that recorded for healing composite in the current study (0.12 MPa.$m^{1/2}$). This may be attributed to the higher percentage of strontium fluoroaluminosilicate glass powders (70 wt%) incorporated in the experimentally prepared resin composite compared to that used in the current study (50 wt%).

The healing ability of HC group was assessed by comparing the fracture toughness K_{IC} of the material before and after healing period (4). In the current study, the average healing efficiency of healing composite was ranging from 16 % to 23 %. These results were comparable to the results by Huyang et al. (2016) (2) which revealed that the healing efficiency was approximately 25 % for healing composite containing 5 wt% of microcapsules. The results of fracture toughness and healing efficiency of HC group after the healing period were confirmed by the FTIR analysis and Scanning electron micrographs.

Regarding the FTIR analysis, it revealed the presence of absorbance peaks related to the silicic acid (H_4O_4Si) and Si-O-Al groups in the HC. These peaks appeared to be similar to that of GIC (24). Typically, in GIC, the setting reaction involves the acid hydrolysis of the glass network. This reaction appeared as an absorbance peak at 846 cm^{-1} which denote the formation of SiO_4 and AlO_4 tetrahedral linked by a Si-O-Al-type bond in the glass network (24). Compared to the FTIR analysis performed immediately after HC preparation (Figure 4a), such peaks were not observed, but an absorbance peak at 730 cm^{-1} (-COOH) was visible.

Concerning the scanning electron micrographs recorded for HC group, the analysis after three days revealed the presence of small patches of a new material formed around the notch area. Similar micrographs were described by Huyang et al. (2016) (2) who reported that a new material have been observed at the crack surface after the healing period was completed.

Accordingly, the null hypothesis was rejected as the incorporation of self-healing microcapsules and fluoroaluminosilicate powder in commercially available flowable composite significantly increased the farcture toughness and healing efficiency following three days water storage. To the best of our Knowledge , such reseach findings may be promising in order to improve the clinical performance of dental composites.

Conclusions

Within the limitation of the current study,

1. Preparing silica based self-healing microcapsules using sol-gel technique yielded a standardized microcapsules with an average diameter of 2.15 μm.
2. Incorporation of 5 wt% self-healing microcapsules containing copolymer of polyacrylic acid and fluoroaluminosilicate into commercially available flowable composite improved the fracture toughness and healing efficiency of the healing composite when compared to as-received flowable composite after three days of storage.
3. The prepared healing composite model in the current study accomplished an autonomous crack healing with materials being used in dental clinics, which is an advantage to accelerate the technology transition from lab to dental clinics.

Recommendations

Further dynamic mechanical testing and clinical investigations are required to evaluate the self-healing composite performance under mastication forces, its clinical performance and survival rate as a restoration.

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Conflict of Interest: The authors have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article

References

1. Wu J, Weir MD, Melo MAS, Xu HHJJod. Development of novel self-healing and antibacterial dental composite containing calcium phosphate nanoparticles. Journal of dentistry. 2015;43(3):317-26.
2. Huyang G, Debertin AE, Sun J. Design and development of self-healing dental composites. Materials & design. 2016;94:295-302.
3. Bekas D, Tsirka K, Baltzis D, Paipetis A. Self-healing materials: A review of advances in materials, evaluation, characterization and monitoring techniques. Composites Part B: Engineering. 2016;87:92-119.
4. Wu J, Xie X, Zhou H, Tay FR, Weir MD, Melo MAS, et al. Development of a new class of self-healing and therapeutic dental resins. Polymer Degradation and Stability. 2019;163:87-99.
5. Galgali G, Schlangen E, van der Zwaag S. Synthesis and characterization of silica microcapsules using a sustainable solvent system template. Materials Research Bulletin. 2011;46(12):2445-9.
6. Sharma A, Alam S, Sharma C, Patnaik A, Kumar SR. Static and dynamic mechanical behavior of microcapsule-reinforced dental composite. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications. 2019;233(6):1184-90.
7. ASTM I. Standard test methods for plane-strain fracture toughness and strain energy release rate of plastic materials. ASTM D5045-99. 2007.

8. Chai H, Wang X, Sun J. Miniature specimens for fracture toughness evaluation of dental resin composites. Dental Materials. 2019;35(2):283-91.
9. Standard A. Standard test methods for plane-strain fracture toughness and strain energy release rate of plastic materials. D5045-96. 1996.
10. Ferracane JL. Placing dental composites—a stressful experience. Operative dentistry. 2008;33(3):247-57.
11. Brown EN, Sottos NR, White SR. Fracture testing of a self-healing polymer composite. Experimental mechanics. 2002;42(4):372-9.
12. Wu J, Weir MD, Melo MAS, Xu HH. Development of novel self-healing and antibacterial dental composite containing calcium phosphate nanoparticles. Journal of dentistry. 2015;43(3):317-26.
13. Mobaraki M, Ghaffari M, Mozafari M. Self-healing polymers for composite structural applications. Self-Healing Composite Materials: Elsevier; 2020. p. 33-51.
14. Yang Z, Hollar J, He X, Shi X. A self-healing cementitious composite using oil core/silica gel shell microcapsules. Cement and Concrete Composites. 2011;33(4):506-12.
15. Zhu DY, Rong MZ, Zhang MQ. Self-healing polymeric materials based on microencapsulated healing agents: From design to preparation. Progress in Polymer Science. 2015;49:175-220.
16. Balazs AC. Modeling self-healing materials. Materials today. 2007;10(9):18-23.
17. Althaqafi KA, Satterthwaite J, Silikas N. A review and current state of autonomic self-healing microcapsules-based dental resin composites. Dental Materials. 2020;36(3):329-42.
18. Huyang G, Sun J. Clinically applicable self-healing dental resin composites. MRS Advances. 2016;1(8):547-52.
19. Berzins DW, Abey S, Costache M, Wilkie CA, Roberts H. Resin-modified glass-ionomer setting reaction competition. Journal of dental research. 2010;89(1):82-6.
20. Ahangaran F, Hayaty M, Navarchian AH, Pei Y, Picchioni F. Development of self-healing epoxy composites via incorporation of microencapsulated epoxy and mercaptan in poly (methyl methacrylate) shell. Polymer Testing. 2019;73:395-403.
21. Aïssa B, Therriault D, Haddad E, Jamroz W. Self-healing materials systems: Overview of major approaches and recent developed technologies. Advances in Materials Science and Engineering. 2012;2012.
22. Yang Y, Zhang H, Zhang J, Wang S, Duan C, He Y. The experiment study of fracture mechanics on self-healing composite material containing microcapsules. Materials Review. 2007;21:143-7.
23. Brown EN, White SR, Sottos NR. Microcapsule induced toughening in a self-healing polymer composite. Journal of Materials Science. 2004;39(5):1703-10.
24. Wan AC, Yap AU, Hastings GW. Acid–base complex reactions in resin-modified and conventional glass ionomer cements. Journal of Biomedical Materials Research: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials. 1999;48(5):700-4.