Performance of Melamine Modified Urea–Formaldehyde Microcapsules in a Dental Host Material

Sonja Then,[1] Gan Seng Neon,[1] Noor Hayaty Abu Kasim[2]

[1]*Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia*
[2]*Department of Conservative Dentistry, University of Malaya, 50603 Kuala Lumpur, Malaysia*

Received 3 August 2010; accepted 26 February 2011
DOI 10.1002/app.34361
Published online 23 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Urea–formaldehyde (UF) microcapsules filled with dicyclopentadiene (DCPD) show potential for making self-healing dental restorative materials. To enhance the physical properties of the capsules, the urea was partially replaced with 0–5% melamine. The microcapsules were analyzed by different microscopic techniques. DSC was used to examine the capsule shell, and the core content was confirmed by ^{1}H NMR spectroscopy. Capsules in the range of 50–300 μm were then embedded in a dental composite matrix consisting of bisphenol-A-glycidyl dimethacrylate (Bis-GMA) and triethylene-glycol dimethacrylate (TEGDMA). Flexural strength, microhardness, and nanoindentation hardness measurements were performed on the light-cured specimens. Optical microscopy (OM) examination showed a random distribution of the microspheres throughout the host material. The incorporation of small amounts of the microcapsules did not affect the performance of the matrix material. Scanning electron microscopy (SEM) analysis revealed excellent bonding of the microcapsules to the host material which is a characteristic of utter importance for maintaining the very good mechanical properties of a dental composite with self-healing ability. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2557–2562, 2011

Key words: microcapsules; dental polymer; mechanical properties; microscopy; self-healing material

INTRODUCTION

Micro-cracking in polymeric materials could lead to a drastic reduction in the performance and useful lifetime of the material. As these microcracks cannot be noticed and repaired on time by manual intervention various groups of researchers have examined systems that can autonomously heal.[1–4] An advanced self-healing system was developed by White et al. at the University of Illinois in the United States.[5] Their material represents microcapsules of a urea-formaldehyde (UF) shell that encapsulated dicyclopentadiene (DCPD) as a healing agent. These microcapsules are embedded in another polymeric matrix along with a selective catalyst. In the event of a crack, the microcapsule shell will break releasing the DCPD into the crack plane which will eventually react with the catalyst to bond the crack planes.

This concept was initially developed for materials in aeronautics. The microcapsules can be customized for other specific applications.[6–9] In particular, the application in dental materials seems highly attractive for the improvement of crack-resistance. The advanced dental composite filling materials show excellent chemical and mechanical properties.[10] However, they are still prone to fatigue failure due to microcracks. Therefore, the application of a self-healing system in a dental restorative material is of utter interest.

The challenge of preparing such a self-healing dental composite system is that the microcapsules must possess sufficient strength to withstand the incorporation process into the host material, yet rupture when the polymeric composite is damaged. The UF microcapsules tend to break during the incorporation into the dental host material. Thus, it is necessary to create microcapsules with a tougher shell. Urea-melamine-formaldehyde polymers are known to have higher bond strength due to its cross-linking ability.[11–13] Therefore, in this study the initial UF shell wall was modified with melamine to enhance the properties of the microcapsules, especially the adhesion to the dental host material.

A series of microcapsules with different melamine amounts in the shell were produced by *in situ* condensation polymerization. The product was inspected by diverse microscopic techniques, whereas thermal analysis was used to verify the shell composition and ^{1}H NMR spectroscopy to analyze the capsule core content. The capsules were

Correspondence to: S. Then (sonja@siswa.um.edu.my).
Contract grant sponsor: Postgraduate Research Grant, University of Malaya.
Contract grant sponsor: Science Fund, Ministry of Science, Technology and Innovation, Malaysia.

then embedded into a dental polymeric host material and their performance in the dental matrix was examined by mechanical tests and microscopy.

EXPERIMENTAL

Materials

The microcapsule wall-forming materials consisted of urea, ammonium chloride and 1,3-dihydroxybenzol (resorcinol) which were acquired from Sigma-Aldrich whereas formalin (37 wt %) was purchased from Systerm and hexamethoxy-methylmelamine (Cymel 303) from Cytec Industries. The core material, DCPD, was obtained from Sigma-Aldrich and used as received. Ethylene maleic anhydride (EMA) copolymer powder with an average molecular weight M_w = 400,000 was used as emulsifier and was purchased from Sigma-Aldrich. 1-octanol was obtained from Sigma-Aldrich, ethanol from HmbG Chemicals, and NaOH from Hoechst. The dental materials were bought from Sigma-Aldrich which included the monomers bisphenol-A-glycidyl dimethacrylate (Bis-GMA) and triethylene-glycol dimethacrylate (TEGDMA) as well as the light-curing system ethyl (4-dimethylamino) benzoate (EDMAB) and camphorquinone (CQ). All chemicals and solvents were of analytical grade except the Cymel 303 which was of technical grade.

Preparation of microcapsules

The microcapsules were prepared by the *in situ* micro-encapsulation procedure adapted from Brown et al.[14] At room temperature, 100 mL distilled water and 25 mL of a 2.5 wt % aqueous solution of EMA copolymer were mixed in a 500 mL glass beaker. Cymel 303 was dissolved in a minimum amount of ethanol. Under agitation by a magnetic stirrer the wall-forming materials urea, melamine (amounts as listed in Table I), 0.25 g ammonium chloride and 0.25 g resorcinol were dissolved in the solution. Then, the pH was raised to 3.50 by drop-wise addition of 10% NaOH solution. After that, the reaction solution was suspended in a temperature-controlled water bath. It was agitated with a mechanical stirrer at 500 rpm driving a three-bladed, 40 mm diameter propeller. Surface bubbles were eliminated by the addition of two drops 1-octanol. Then, 30 mL DCPD was added to form a suspension of fine droplets. After stabilization, 6.34 g formalin was added. The mixture was covered with aluminum foil and the temperature was raised to 55°C at a rate of 1.5°C/min. After 4 h the reaction slurry was removed and allowed to cool down. The suspension was filtered and rinsed with water and ethanol. The dry capsules were separated by sieving through precision test sieves (Endecotts, certified acc. to BS 410, ISO 3310).

TABLE I
Urea and Melamine Parts for the Microcapsule Synthesis

Sample No.	Cymel (%)	Cymel (g)	Ureain (g)
1	0	0.000	2.500
2	0.5	0.025	2.488
3	1	0.053	2.475
4	2	0.105	2.450
5	3	0.158	2.425
6	4	0.210	2.400
7	5	0.263	2.375

The resulting microcapsules showed diameters in the range of 50–500 μm.

Specimen preparation

The monomers Bis-GMA and TEGDMA were mixed together in the ratio of 7 : 3 by weight. Then, in a dark environment, the initiator system consisting of 2.3 wt % EDMAB and 0.7 wt % CQ were added. The ingredients were homogeneously mixed and degassed in an ultrasonic bath to obtain the dental host material. The microcapsules were carefully added and the mixture was sonicated for another 30 min to remove any air bubble. Two different weight percentages of microcapsules were incorporated. In the first set, a series of 6% microcapsules of the size fraction 50–300 microns were incorporated. In the second set, a series of 3% microcapsules were embedded. The material containing the capsules with a pure UF shell served as a reference next to a sample of the virgin host material (without microcapsules).

The prepared matrix resin was poured into cylindrical metal molds (dimensions: h = 2 mm, d = 8 mm) for hardness measurements after curing. For the 3-point-bending tests bar shaped specimens were prepared (dimensions: l = 25 mm, h = 2 mm, t = 2 mm) according to ISO 4049 : 2000.[15] Each flexural strength specimen was irradiated for 100 s in total from either side using a halogen curing light (Dentsply), whereas the hardness specimens were irradiated for 60 s from each side. After the specimens were removed from the molds any flash was carefully trimmed away. All samples were stored in distilled water at 37 ± 1°C for 24 h before testing.

Characterization of microcapsules

The shape of the microcapsules was examined with a hand-held digital microscope (AnMo Electronics), whereas the shell morphology was examined by optical microscopy (OM, Leica) and Scanning electron microscopy (SEM; FEI Quanta 250 FEG, low vacuum). For the SEM analysis, microcapsules were carefully glued on a carbon tape; part of the capsules was ruptured with a razor blade to facilitate shell membrane inspections. To determine the core

content the capsules were rinsed with acetone to wash off any residual material. The dry capsules were ground with a mortar and extracted with deuterium acetone. The ^{1}H NMR spectrum was recorded on a 400 MHz Bruker FT NMR system.

To differentiate the melamine-modified shell from the neat UF material, DSC analysis on a Perkin–Elmer Diamond was performed. Therefore, microcapsules of a pure UF shell and the 5% melamine modified UF shell were ground with a pestle in a mortar each. The crushed capsule material was collected and intensively washed with acetone. The heat flow of the dried powders was then recorded from 35 to 350°C at a heating rate of 10°C/min.

After the incorporation of the microcapsules into the dental host material, the distribution of the capsules was examined by OM. For the study of the microcapsule shell adhesion to the host material a test specimen containing capsules of a pure UF shell and another specimen containing capsules of the 5% melamine modified UF shell were ruptured. The interface between capsule and host matrix on the broken surfaces were inspected by SEM.

Mechanical testing

The flexural strength measurement was performed according to ISO 4049: 2000[15] using a Shimadzu AG-X high precision universal testing machine. The setup consisted of two rods (2 mm in diameter), mounted parallel with 20 mm distance, on which the test specimen was placed. The load was applied to the specimen at a cross-head speed of 0.75 ± 0.25 mm/min until the specimen fractured. Eight specimens of each sample were measured. Vickers hardness tests were carried out on a Shimadzu HMV-2 microhardness measuring machine according to ASTM E 384—89:1990.[16] Measurements were obtained from five specimens and 25 indentations were analyzed per sample. The nanoindentation hardness was determined on a dynamic ultra micro hardness tester (Shimadzu DUH-211) using a Berkovich indenter (triangular pyramid, 115°) at a test force of 50 gf (490.33 mN) and a hold time of 5 s. Nine indentations were measured on each specimen.

RESULTS AND DISCUSSION

Analysis of microcapsules

The successful preparation of microcapsules was confirmed for each sample by digital microscopy. Microscopic images showed a variety of spherical microcapsules of different diameter. Both the OM and SEM confirmed the spherical shape of the capsules with its typical rough porous outer shell [Fig. 1(a)] that is formed by the agglomeration of

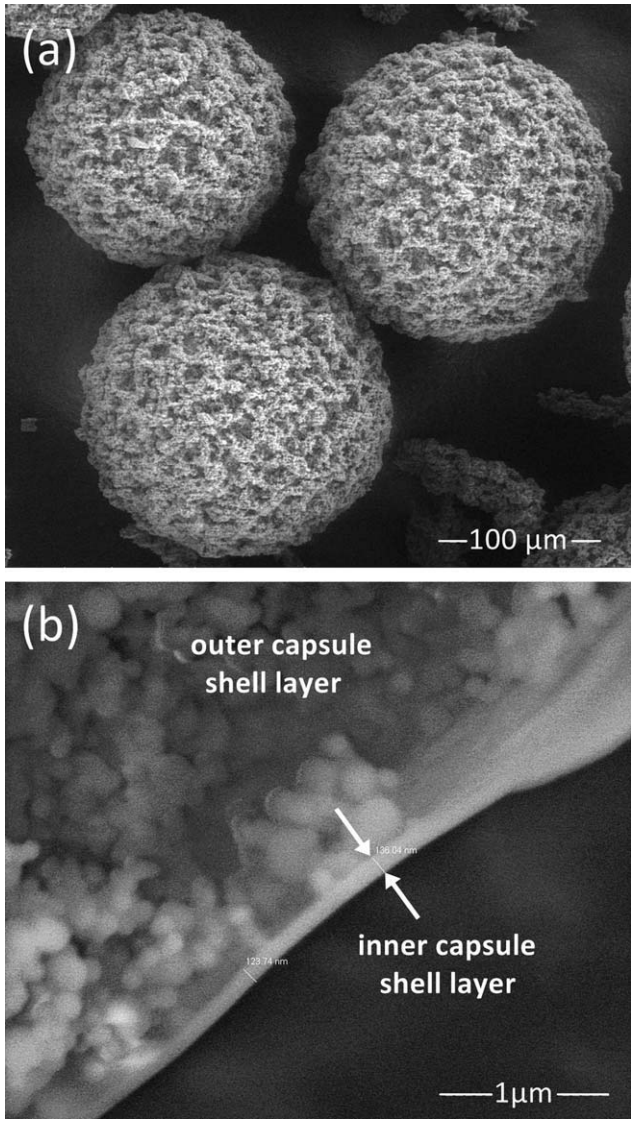

Figure 1 SEM images of melamine-modified UF microcapsules displaying (a) spherical capsules with their rough porous outer shell and (b) the smooth inner shell wall on which agglomerations of UF nanoparticles are sticking that build the outer shell layer.

numerous nano-particles that deposit on the smooth inner capsule shell layer [Fig. 1(b)].[17] There was no visual difference between the pure UF sample and the 5% melamine modified capsule shell.

The spectra that was obtained from ^{1}H NMR analysis of the extracted core material showed the characteristic peaks of DCPD at 1.17 ppm (d,1H); 1.30 ppm (d,1H); 1.45–1.52 ppm (m,1H); 1.97–2.05 ppm (m,1H); 2.56–2.66 ppm (m,2H); 2.72 ppm (s,1H); 3.06 ppm (m,1H); 5.28–5.33 ppm (m,2H); 5.74–5.83 ppm (m,2H).

Figure 2 illustrates the heat flow curves of the capsules with the pure UF shell in comparison with the spectra of the 5% melamine modified sample that were obtained from the DSC measurements. Both

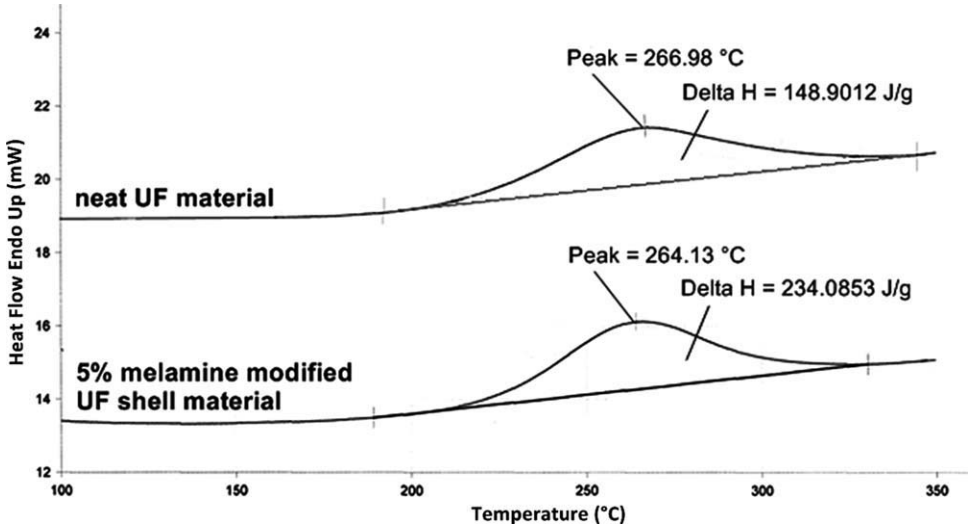

Figure 2 DSC curves of the melamine-modified UF microcapsule shell material in comparison with the neat UF material.

spectra showed endothermic peaks of a melting process. The melting temperature (T_m) of the UF material was 267°C and for the melamine modified sample T_m was reached at 264°C. A distinct differentiation was provided by the enthalpy of melting (ΔH_m) which is calculated from the peak area. ΔH_m was considerably higher for the melamine modified samples (234 J/g) than for the UF sample (149 J/g). This might be an indication for the higher amount of crystallinity with 5% of the urea being replaced with melamine, resulting in an increased ΔH_m.

Microscopic characterization of microcapsules in dental material

Both OM and SEM revealed a random distribution of the microcapsules in the polymeric host material. The OM images in Figure 3 illustrate two different amounts of the 5% melamine modified UF microcapsules embedded in a dental matrix.

Images obtained from SEM (Fig. 4) show that the rough exterior shell wall of the embedded melamine modified UF microcapsule is infiltrated by the matrix methacrylates. This is highly advantageous for better adhesion of the capsules to the host material and increases the probability of the capsule rupture on crack intrusion. There was no clear difference between the bonding ability of the pure UF microcapsule shell in comparison with the 5% melamine modified shell from the SEM images.

Mechanical properties of dental material containing microcapsules

Overall, the mechanical properties were not adversely affected by the incorporation of the microcapsules. The flexural strength of the virgin material

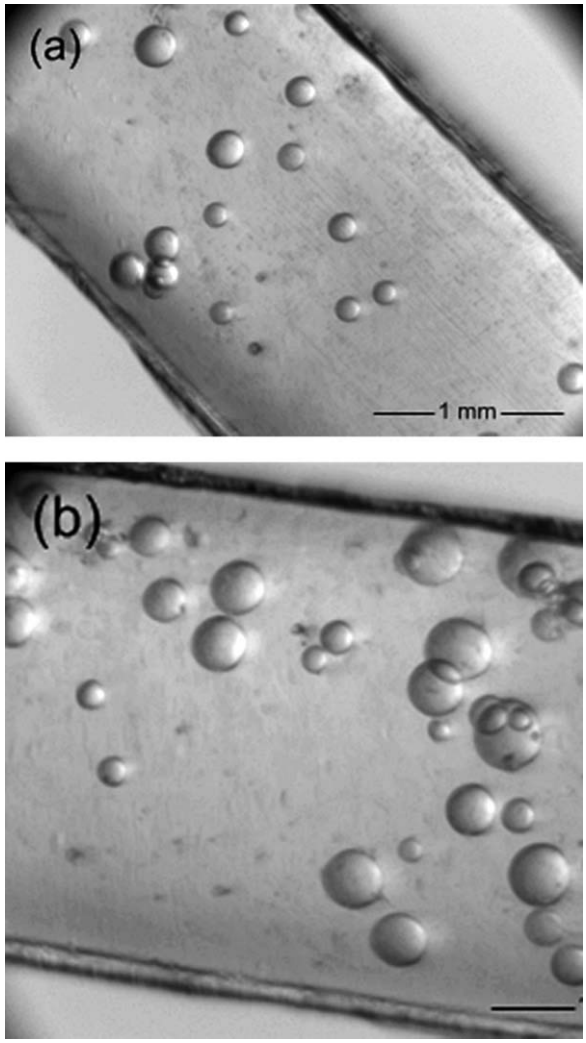

Figure 3 Optical micrographs of melamine-modified UF microcapsules embedded in a dental host material showing (a) 3 wt % and (b) 6 wt % capsules randomly distributed throughout the material.

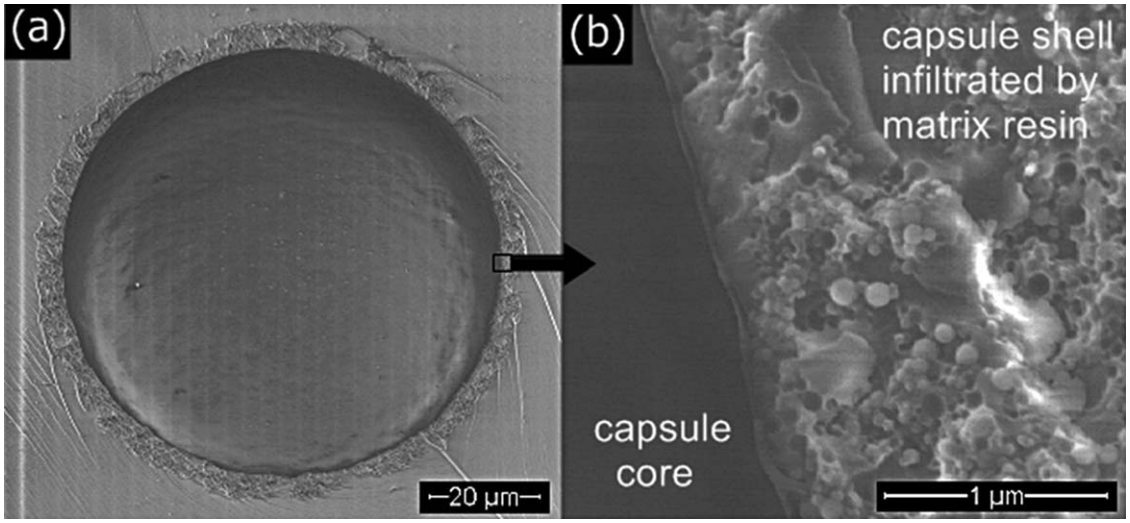

Figure 4 SEM images of (a) an embedded melamine modified UF microcapsule in a dental matrix, and (b) the interface of the microcapsule and the dental matrix with the microcapsule outer shell penetrated by the host material.

(106.3 ± 19.8 MPa) was less than 10% reduced after the incorporation of up to 6% UF/DCPD microcapsules as it is illustrated in Figure 5. For instance, after the incorporation of 3% UF/DCPD microcapsules the high strength values were maintained with 105.1 ± 24.8 MPa [Fig. 5(a)], whereas the incorporation of 6% UF/DCPD microcapsules resulted in an average flexural strength value of 64.6 ± 23.5 MPa [Fig. 5(b)]. The melamine modification of the UF capsule shell (0.5–5% of the urea replaced by melamine) did not significantly increase the flexural strength in neither of the two test series with values around 80 MPa.

The microhardness measurements confirmed the results obtained from the three-point-bending test. The Vickers hardness number (VHN) of the initial material (30.7 ± 1.6 HV) was hardly affected by the incorporation of 3% and 6% microcapsules with average values in the range of 24.1–25.8 HV and 21.7–28.8 HV, respectively. There was no relevant trend in the VHN within the test series of the different melamine modified microcapsule samples.

In contrary to the results of microhardness and three-point-bending measurements, the nanoindentation test showed a lower average hardness for the virgin material with 178.4 ± 8.3 MPa as displayed in Figure 6. The peak value was achieved by the sample containing 1% melamine with 238.1 ± 26.5 MPa, followed by the 5% sample with 223.7 ± 36.0 MPa and 194.8 ± 28.3 MPa for the 2% sample whereas the pure UF capsules showed the lowest average nanohardness (149.7 ± 7.2 MPa). Considering the high standard deviation which increased with raising hardness values using the nanoindentation test method, it can be concluded that the melamine modification does not have a significant impact on the hardness of the dental material. Generally, the nanoindentation test showed that the incorporation of 6% microcapsules does not reduce the good initial hardness of the dental material which proofs the results

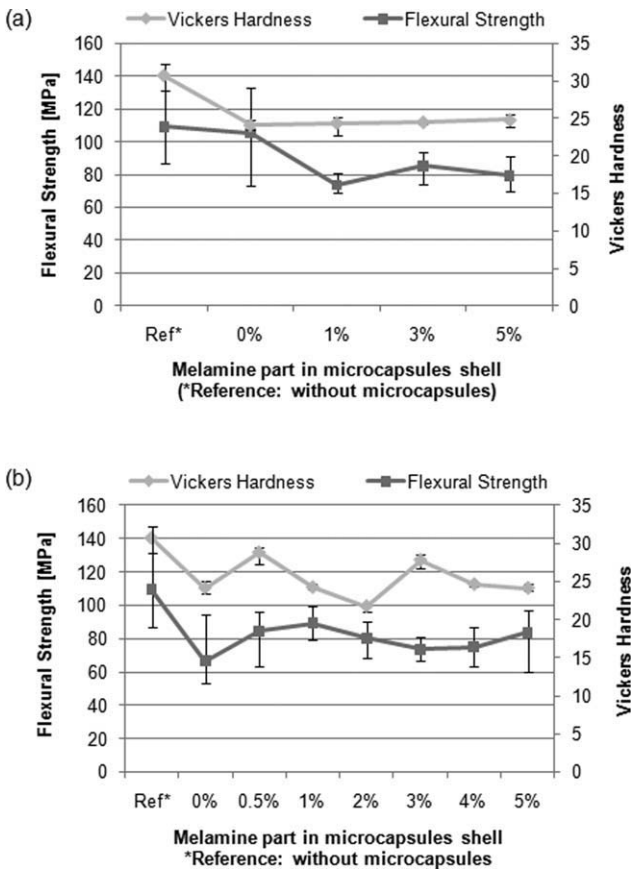

Figure 5 Flexural Strength and Vickers Hardness of a dental polymeric material with (a) 3 wt % microcapsules and (b) 6 wt % microcapsules embedded, displaying the influence of different melamine amounts in the capsule shell.

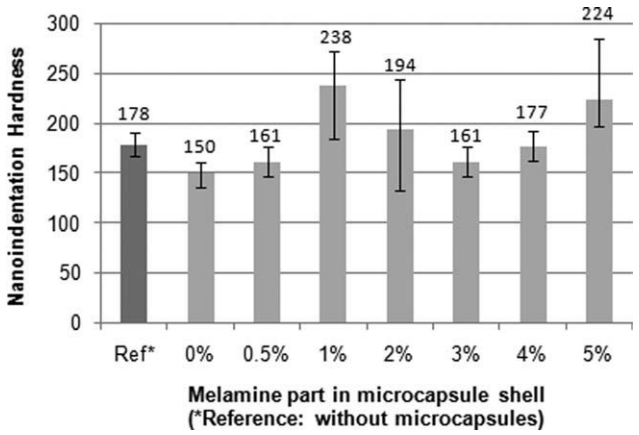

Figure 6 Nanoindentation hardness of dental polymeric material containing 6 wt % UF microcapsules with different melamine amounts in the capsule shell.

obtained from the flexural strength and microhardness measurements.

CONCLUSIONS

A series of microcapsules with varying amounts of melamine in the UF shell was produced to develop a self-healing dental composite material. Two different amounts of microcapsules were incorporated into the dental host materials, which were then inspected by microscopy as well as mechanical tests. OM showed that the microcapsules were randomly distributed throughout the material which increases the probability that an upcoming crack encounters the capsules in a self-healing system. SEM analysis confirmed the very good adhesion of the capsule shell to the dental host material which is a requirement of utter importance to maintain the excellent mechanical properties of the virgin dental material and to guarantee that the capsule shell breaks upon crack intrusion. Eventually, mechanical measurements revealed that the good characteristics of the original material were not affected after the incorporation of up to 6% UF/DCPD microcapsules. The partial substitution of the urea in the capsule shell by melamine up to 5% did not show any significant impact on the mechanical properties of the dental matrix.

In general, this research provides a novel approach to modify the UF capsule shell for the specific application in a methacrylate based polymeric matrix material. Further changes in the microcapsule composition to customize them for the development of a self-healing dental restorative composite material will be examined in our future studies.

References

1. Dry, C. Compos Struct 1996, 35, 263.
2. Li, V. C.; Lim, Y. M.; Chan, Y. W. Compos Part B 1998, 29, 819.
3. Pang, J. W. C.; Bond, I. P. Compos Part A 2005, 36, 183.
4. Thao, T. D. P.; Johnson, T. J. S.; Tong, Q. S.; Dai, P. S. The IES J Part A: Civil & Structural Engineering 2009, 2, 116.
5. White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R. Nature 2001, 409, 794.
6. Sliwka, W. Angew Chem 1975, 87, 556.
7. Markus, A.; Linder, C. In Microencapsulation: Methods and Industrial Applications, 2nd ed.; Benita, S., Ed.; Marcel Dekker: New York, 1996; Vol.158.
8. Arshady, R.; Guyot, A. Functional Polymer Colloids and Microparticles: Microspheres, Microcapsules and Liposomes; Citus Books: London, 2002; Vol.4.
9. Ghosh, S. K.; Functional Coatings by Polymer Microencapsulation; Wiley-VCH: Weinheim, 2006.
10. Manhart, J.; Kunzelmann, K. H.; Chen, H. Y.; Hickel, R. Dent Mater 2000, 16, 33.
11. Tohmura, S.; Inoue, A.; Sahari, S. H. J Wood Sci 2001, 47, 451.
12. Schwarz, O. Kunststoffkunde, 4th ed.; Vogel Verlag: Wuerzburg, 1992.
13. Pizzi, A.; Mittal, K. L. Handbook of Adhesive Technology, 2nd ed.; Marcel Dekker: New York, 2003.
14. Brown, E. N.; Kessler, M. R.; Sottos, N. R.; White, S. R. J Microencapsulation 2003, 20, 719.
15. ISO 4049:2000. Dentistry—Polymer-Based Filling, Restorative and Luting Materials; International Organization for Standardization: Geneva.
16. ASTM E 384-89:1990. Standard Test Method for Microhardness of Materials. Annual book of ASTM Standards, E04.05; American Society for Testing and Materials: Philadelphia.
17. Blaiszik, B. J.; Caruso, M. M.; McIlroy, D. A.; Moore, J. S.; White, S. R.; Sottos, N. R. Polymer 2009, 50, 990.