

**SELF-HEALING POLYMERIC MATERIALS FOR
POTENTIAL DENTAL APPLICATION**

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ABSTRACT

Poly(urea-formaldehyde) (PUF) microcapsules that enclose dicyclopentadiene (DCPD) were successfully prepared by *in situ* polymerization. The effect of diverse process parameters and concentrations of ingredients on the product yield and quality was investigated. After optimizing the procedure high yields of microcapsules were obtained (up to 89%) which appeared in the form of a free-flowing white powder. The morphology of the microcapsules was observed by digital microscopy, optical microscopy (OM), and field emission gun scanning electron microscopy (FESEM). FTIR and ¹H-NMR were employed to analyze the chemical structure and content of the core material. The thermal properties were characterized utilizing DSC and TGA. The microcapsules could be incorporated into another polymeric host material. In the event the host material cracks due to excessive stress or strong impact, the microcapsules would rupture to release the DCPD, which could polymerize to repair the crack, thus autonomously heal the material.

To enhance the properties of the microcapsule shell, the urea was partially replaced with up to 5% melamine. Different microscopic techniques, FTIR spectroscopy and DSC were employed to examine the capsule shell, whereas the core content was confirmed by ¹H-NMR. Capsules in the range of 50-300 μm were then embedded in a light curable dental composite matrix consisting of bisphenol-A-glycidyl dimethacrylate (Bis-GMA) and triethylene-glycol dimethacrylate (TEGDMA). Two different amounts (3 wt% and 6 wt%) of microcapsules were embedded into the dental host material and their performances were evaluated through mechanical tests. OM examination of the light-cured specimens showed a random distribution of the microspheres throughout the host material, whereas FESEM

analysis revealed excellent bonding of the microcapsules to the host material. These characteristics are of utter importance for maintaining the very good mechanical properties of a dental composite with self-healing ability. Flexural strength, microhardness and nanoindentation hardness measurements proved that the addition of the microcapsules did not affect the mechanical properties of the virgin matrix material. The substitution of the urea with small amounts of melamine in the capsule shell has improved the hardness of the microcapsules and made it easier to mix with the viscous host material before light curing.

Finally, the encapsulation of epoxy resins was studied. PUF microcapsules were prepared incorporating the commercially available Epikote 828 (diglycidylether of bisphenol-A, DGEBA) diluted in n-butyl glycidyl ether (BGE). Proton NMR spectroscopy verified the presence of the epoxy core. DSC result has shown the onset of degradation of PUF/epoxy microcapsules was above 170°C. FESEM showed that the PUF/epoxy microcapsules adhered well to the epoxy matrix resin.

In summary, this research work scrutinized the microcapsule based self-healing system for the potential application in dental polymeric materials. The findings that were obtained during the course of this study are significant for the further development of a self-healing restorative composite.

ABSTRAK

Mikrokapsul poli(urea-formaldehid) (PUF) yang mengandungi disiklopentadiena (DCPD) telah berjaya dihasilkan melalui proses pempolimeran *in situ*. Kepelbagaian kesan parameter proses dan kepekatan reaktan terhadap hasil dan kualiti produk telah disiasat. Setelah pengoptimuman prosedur pempolimeran, mikrokapsul terhasil adalah dalam peratusan yang tinggi (setinggi 80%) dan terjelma dalam bentuk serbuk putih yang “free-flowing”. Morfologi mikrokapsul dianalisis menggunakan mikroskop digital, mikroskop optik dan “field emission gun scanning electron microscopy” (FESEM). FTIR dan ¹H-NMR digunakan untuk menganalisis struktur kimia dan kandungan teras mikrokapsul. Analisis terma dijalankan menggunakan DSC dan TGA. Mikrokapsul ini boleh dimasukkan kedalam bahan polimer hos yang lain. Apabila berlaku retakan pada material hos oleh sebab stres atau impak yang kuat, mikrokapsul akan pecah dan DCPD yang terkandung didalamnya akan terlepas keluar dan seterusnya boleh mengalami proses pempolimeran untuk membaiki retakan tersebut. Justeru material tersebut pulih secara automatik.

Untuk menambah baik ciri-ciri dinding mikrokapsul, urea tersebut digantikan sebahagiannya dengan 5% melamin. Teknik mikroskopik, spektroskopi FTIR dan DSC yang berbeza pula digunakan untuk mengkaji dinding kapsul tersebut. Kandungan teras mikrokapsul pula disahkan dengan menggunakan H-NMR. Kapsul dalam lingkungan saiz 50-300µm kemudiannya dimasukkan kedalam komposit matriks yang mengandungi bisfenol-A-glisidil dimetakrilat (Bis-GMA) dan trietilena-glikol dimetakrilat (TEGDMA). Dua kandungan mikrokapsul yang berbeza (3% dan 6%) dimasukkan ke dalam material hos pergigian dan prestasinya diuji melalui ujian-ujian mekanikal. Pemeriksaan OM terhadap bahan spesimen “light-cured” menunjukkan

taburan mikrokapsul yang pelbagai diseluruh bahagian dalam bahan hos, manakala FESEM pula menunjukkan perlekatan yang baik diantara mikrokapsul dan bahan hosnya. Ciri-ciri ini merupakan kunci utama bagi mendapatkan ciri atau prestasi kekuatan mekanikal yang baik dalam sesuatu bahan komposit pergigian dengan kebolehan terbaik-pulih (self-healing). Ujian-ujian terhadap kekuatan fleksural, kekerasan mikro dan indentasi-nano membuktikan bahawa penambahan mikrokapsul kedalam bahan hos tidak memberi kesan terhadap ciri-ciri asal bahan matriks. Sebaliknya, penukargantian urea kepada sejumlah kecil melamin dalam dinding kapsul telah mempertingkatkan kekerasan dinding mikrokapsul dan mempermudahkannya untuk tercampur dengan bahan hos yang likat sebelum di “light-cure”.

Akhirnya, kajian dijalankan terhadap pengkapsulan resin epoksi. Mikrokapsul PUF disediakan dengan memasukkan bahan komersial Epikote 828 (bisfenol-A diglisidil eter, DGEBA) yang dicairkan dalam n-butyl glisidil eter (BGE). Spektroskopi proton NMR mengesahkan kehadiran teras epoksi. Analisis DSC menunjukkan degradasi onset mikrokapsul PUF/epoksi adalah melebihi 170°C. Analisis FESEM menunjukkan matriks resin terkandung dengan baik didalam mikrokapsul PUF/epoksi.

Konklusinya, kerja penyelidikan ini adalah mengenai sistem terbaik-pulih berasaskan mikrokapsul sebagai potensi aplikasi dalam bahan polimer pergigian. Hasil kajian ini adalah signifikan bagi terus menyelidik dan membangunkan bahan komposit terbaik-pulih bagi tujuan pembaikpulihan.

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TABLE OF CONTENTS

	Page
DECLARATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGEMENTS	vii
TABLE OF CONTENTS	ix
LIST OF FIGURES	xvii
LIST OF TABLES	xxvi
LIST OF ABBREVIATIONS	xxx
LIST OF SYMBOLS AND UNITS	xxxii

CHAPTER I: GENERAL INTRODUCTION

1.1	Introduction	1
1.2	Aim of the Present Investigation	3
1.3	Overview of the Dissertation	4
1.4	Basic Considerations for the Development of a Self-Healing Dental Restorative Material	5
1.4.1	General Requirements on the Self-Healing Composite System	5
1.4.2	Requirements on the Healing Monomer	6
1.4.3	Requirements on the Specific Catalyst for the Healing Monomer	6
1.4.4	Requirements on the Microcapsule Shell	7

CHAPTER II: LITERATURE REVIEW

2.1	Dental Composites	8
2.1.1	Introduction	8
2.1.2	Acrylate-Based Resin Matrix	11
2.1.3	Curing System for Acrylic Resin	14
2.1.4	Low-Shrinkage Epoxy-Based Resin Matrix	15
2.2	Epoxy Resins in Industrial Application	18
2.2.1	Introduction	18
2.2.2	Reactive Diluents	19
2.2.3	Curing Agents	19
2.2.4	Polyaddition Reaction of Epoxide and Amine	20
2.3	Self-Healing Polymeric Materials	22
2.3.1	Introduction	22
2.3.2	Microcapsule-Based Self-Healing Concept	24
2.3.3	The Healing-Compound	25
2.3.4	Ring-Opening Metathesis Polymerization (ROMP)	25
2.3.5	ROMP Catalysts	26
2.4	Microencapsulation	28
2.4.1	Introduction	28
2.4.2	Encapsulation Techniques	29
2.4.3	Microencapsulation by <i>in situ</i> Emulsion Polymerization	31
2.4.4	Urea Formaldehyde Shell Formation by Condensation Polymerization	32
2.4.5	Urea-Melamine-Formaldehyde (UMF) Resin	34
2.5	Mechanical Testing of Dental Material	35

2.5.1	Introduction	35
2.5.2	Flexural Strength	36
2.5.3	Modulus of Elasticity	38
2.5.4	Toughness	40
2.5.5	Hardness	40
	2.5.5.1 Vickers Microhardness	42
	2.5.5.2 Nanoindentation Hardness	44

**CHAPTER III: MICROENCAPSULATION OF THE HEALING MONOMER
IN A POLY(UREA-FORMALDEHYDE) SHELL**

3.1	Introduction	47
3.2	Materials	47
3.3	Method	48
	3.3.1 General Procedure for PUF/DCPD Microcapsule Preparation	48
	3.3.2 Study of Microencapsulation Process Parameters	50
	3.3.2.1 Reaction Time	51
	3.3.2.2 Initial pH	51
	3.3.2.3 Product Treatment with Diverse Solvents	51
	3.3.2.4 Variation of Formaldehyde-Urea Ratio	52
	3.3.3 Microencapsulation of Alternative Core Monomers	53
	3.3.4 Product Analysis	53
	3.3.4.1 Microcapsule Size and Yield Evaluation	53
	3.3.4.2 General Analysis by Digital and Optical Microscopy	54
	3.3.4.3 Examination of Microcapsule Shell by Field Emission Scanning Electron Microscopy (FESEM)	54

3.3.4.4	Thermal Stability of Microcapsules by Thermogravimetric Analysis (TGA)	55
3.3.4.5	Verification of Microcapsule Core Content by Different Analytical Methods	55
	<i>a. Fourier Transform Infrared (FTIR) Spectroscopy</i>	56
	<i>b. Differential Scanning Calorimetry (DSC)</i>	57
	<i>c. Nuclear Magnetic Resonance (NMR) Spectroscopy</i>	57
3.3.5	Shelf-Life Test	57
3.4	Results and Discussion	58
3.4.1	Impact of Selected Parameters on Product	58
3.4.1.1	Reaction Time	58
3.4.1.2	Initial pH	60
3.4.1.3	Solvents for Microcapsule Separation	61
3.4.1.4	Effect of Formaldehyde-Urea Ratio on Microcapsule Shell Formation	64
3.4.2	Microcapsule Yield and Size Fractions	66
3.4.3	Microcapsule Analysis by Microscopic Methods	68
3.4.3.1	Product Characterization by Digital Microscopy	68
3.4.3.2	Shape and Shell Thickness by Optical Microscopy (OM)	68
3.4.3.3	Shell Composition and Morphology by FESEM-EDX	69
3.4.3.4	Membrane Thickness by FESEM	71
3.4.4	Thermal Stability of Microcapsules by TGA	72
3.4.5	Verification of Encapsulated DCPD	73

3.4.5.1 FTIR Spectroscopy of Microcapsules and PUF Shell	
Material	73
3.4.5.2 DSC of Microcapsules and PUF Shell Material	78
3.4.5.3 Proton NMR Spectroscopy of Core Monomer	79
3.4.6 Encapsulation of Dental Monomers	80
3.4.7 Shelf-Life of Microcapsules	81
3.4.7.1 Discolouration and Flowing Behaviour after Storage	82
3.4.7.2 Chemical Stability of the Core Monomer	83
3.4.7.3 Physical Stability of the Microcapsule Shell	83
3.5 Summary and Conclusions	85

**CHAPTER IV: MELAMINE MODIFICATION OF THE PUF
MICROCAPSULE SHELL AND INCORPORATION
OF THE MICROCAPSULES IN A DENTAL MATRIX**

4.1 Introduction	87
4.2 Materials	87
4.3 Method	88
4.3.1 Preparation of Melamine Modified PUF/DCPD Microcapsules	88
4.3.2 Characterization of Melamine Modified Microcapsules	89
4.3.2.1 General Analysis	89
4.3.2.2 Determination of Shell Composition	89
4.3.2.3 Examination of Shell Morphology	90
4.3.3 Incorporation of Microcapsules in Dental Host Material	90
4.3.3.1 Specimen Preparation	91

4.3.3.2	Examination of Embedded Microcapsules by Microscopy	92
4.3.3.3	Mechanical Tests	93
4.4	Results and Discussion	94
4.4.1	Microcapsule Analysis	94
4.4.1.1	Yield, Quality and Shell Morphology	94
4.4.1.2	Verification of Core Content	94
4.4.1.3	Shell Composition by FTIR Spectroscopy	95
4.4.1.4	Differentiation of Shell Composition by Thermoanalytical Methods	96
4.4.2	Characterization of Microcapsule Embedded Polymeric Material	98
4.4.2.1	Microcapsule Distribution in the Host Material	98
4.4.2.2	Inspection of Microcapsule-Matrix Interface by FESEM	99
4.4.2.3	Flexural Strength	100
4.4.2.4	Vickers Hardness by Microindentation Measurement	102
4.4.2.5	Nanoindentation Hardness	102
4.4.2.6	Young's Modulus	105
4.5	Summary and Conclusion	107

**CHAPTER V: PREPARATION OF PUF MICROCAPSULES
CONTAINING EPOXY RESIN**

5.1	Introduction	109
5.2	Materials	110

5.3	Method	110
5.3.1	Microencapsulation of Epoxy Compounds	110
5.3.1.1	Two-Step Encapsulation Procedure	111
5.3.1.2	Single-Step Encapsulation Procedure	113
5.3.1.3	Product Aftertreatment	115
5.3.1.4	Encapsulation of Amine Curing Agent	116
5.3.2	Analysis of PUF/Epoxy Microcapsules	117
5.3.2.1	Product Yield and Quality	117
5.3.2.2	Examination of Microcapsules by Microscopic Methods	117
5.3.2.3	Determination of Microcapsule Core Content by ¹ H-NMR Spectroscopy	117
5.3.2.4	Thermal Analysis of the Microcapsules	118
5.3.3	Incorporation of PUF/Epoxy Microcapsules in Epoxy Matrix	119
5.3.4	Examination of Embedded Microcapsules by FESEM	119
5.4	Results and Discussion	119
5.4.1	Microcapsule Yield, Size and Shape	120
5.4.2	FESEM of Microcapsule Shell	122
5.4.3	Verification of Epoxy Core by ¹ H-NMR Spectroscopy	122
5.4.4	Characterization of the Microcapsules by DSC	124
5.4.5	Incorporation of PUF/Epoxy Microcapsules in Epoxy Matrix	125
5.4.6	Adhesion of PUF Microcapsule Shell to Epoxy Host Resin	126
5.5	Summary and Conclusion	126

CHAPTER VI: CONCLUSIONS AND FUTURE WORK

6.1	Conclusions	128
6.2	Participation in Conferences and Exhibitions	130
6.3	Suggestions for Future Work	132

REFERENCES	136
-------------------	-----

APPENDIX A: Raw Data of FESEM – EDX Analysis	151
---	-----

APPENDIX B: Thermograms of Shelf-Life Test	155
---	-----

APPENDIX C: Raw Data of Mechanical Measurements	156
--	-----

APPENDIX D: Publications	167
---------------------------------	-----

LIST OF FIGURES

	Page
Figure 2-1	10
Spiro ortho carbonates: (a) general structural formula and (b) example of a spiro ortho carbonate as possible compound of a dental composite	
Figure 2-2	10
Structural formula of two diepoxide monomers that could be part of an epoxy-based dental matrix resin: (a) BADGE and (b) ECHM-ECHC	
Figure 2-3	10
Examples of different types of 2-vinylcyclopropane monomers that might be interesting for the application in a novel dental composite matrix: (a) asymmetric substituted, (b) spirocyclic, and (c) difunctional vinylcyclopropane	
Figure 2-4	13
Chemical structures of common dental monomers: (a) Bis-GMA, (b) TEGDMA, and (c) UDMA	
Figure 2-5	17
Silorane monomer	
Figure 2-6	18
Structure of the common epoxy resin DGEBA	
Figure 2-7	19
Structural formula of BGE which is commonly used in industry as a reactive diluent monomer to reduce the viscosity of epoxy resins	
Figure 2-8	20
Illustration of the polyaddition reaction of an epoxy-amine system	
Figure 2-9	21
Diepoxy molecules and diamine molecules can react and tie together to form a heavily crosslinked polymer network	

Figure 2-10	Illustration of a self-healing approach: (a) microcapsules filled with a healing monomer and a selective catalyst embedded in a dental host material; (b) an approaching crack ruptures microcapsules, releasing the healing monomer into the crack plane; (c) contact of the healing monomer with the catalyst, triggering polymerization and mending the crack	25
Figure 2-11	ROMP of DCPD creating a crosslinked polymer network of poly(dicyclopentadiene) (pDCPD)	26
Figure 2-12	ROMP catalysts: (a) Grubbs 1 st generation, (b) Grubbs 2 nd generation, (c) Hoveyda-Grubbs 1 st generation, and (d) Hoveyda-Grubbs 2 nd generation	27
Figure 2-13	Droplets of the core material built by vigorous agitation; the shell materials move to the interface and react to form the shell around the microsphere (retrieved from http://www.swri.org/3pubs/BROCHURE/D01/mne.htm , 09-09-2010)	31
Figure 2-14	Formation of mono-, di-, and trimethylolurea by the addition of formaldehyde to urea in the first stage of the UF resin formation	32
Figure 2-15	Illustration of the addition of formaldehyde to melamine to form methylol derivatives, e.g. trimethylol melamine and hexamethylol melamine	34
Figure 2-16	(a) Simplified representation of the melamine polymer and (b) possible network structure	35

Figure 2-17	Illustration of (a) a three-point-bending test set-up and (b) the flexural strength data obtained from the measurement in a stress-strain diagram	37
Figure 2-18	Calculation of the modulus of elasticity from the slope of the linear part of the stress-strain graph	39
Figure 2-19	Fracture toughness measured as the total area under a plot of tensile stress versus tensile strain	40
Figure 2-20	Images of a microhardness measurement showing (a) the Vickers indenter placed above a test specimen and (b) a micrograph of an indentation imprint on a dental polymeric material produced by a Vickers indenter	43
Figure 2-21	(a) Illustration of the measurement principle of a dynamic UMH tester and (b) indentation impression produced during nanoindentation hardness testing of a dental polymeric material using a Berkovich indenter	45
Figure 2-22	Diagram of a load-unload curve obtained from a nanoindentation measurement showing important parameters for the calculation of the test results	46
Figure 3-1	Setup for the preparation of PUF/DCPD microcapsules by <i>in situ</i> oil-in-water emulsion polymerization	49
Figure 3-2	(a) Reaction slurry after the synthesis of PUF/DCPD microcapsules which was rinsed, filtered, and dried to obtain (b) the product in the form of a free-flowing white powder	50

Figure 3-3	Influence of the reaction time on the PUF/DCPD microcapsule formation displayed in images obtained from digital microscopy. Reaction time: (a) 1 hour, (b) 2 hours, (c) 3 hours, and (d) 4 hours	59
Figure 3-4	Digital micrographs of PUF/DCPD microcapsules prepared at different initial pH-values: (a) pH 3.1, (b) pH 3.3, (c) pH 3.5, and (d) 3.7	61
Figure 3-5	Micrographs of PUF/DCPD microcapsules demonstrating the effect of different solvents on the product	62
Figure 3-6	Micrographs of PUF/DCPD microcapsules illustrating the impact of the exposure to selected solvents for 2 hours	63
Figure 3-7	Optical micrographs of PUF/DCPD microcapsules produced with varying formaldehyde-urea molar ratio in the capsule shell: (a) 1.1, (b) 1.5, (c) 1.9 and (d) 2.3	65
Figure 3-8	Digital microscopy images showing PUF/DCPD microcapsules obtained from two different formaldehyde-urea molar ratios: (a) 1.5 and (b) 2.3	66
Figure 3-9	Images obtained from the miniature digital microscope showing spherical PUF/DCPD microcapsules at the two possible magnifications: (a) 5 x and (b) 200 x	68
Figure 3-10	Optical micrographs of (a) spherical PUF/DCPD microcapsule displaying the inner shell membrane as a dark clear line surrounded by an uneven outer layer, and (b) the thickness measurement of the two shell layers	69

Figure 3-11	FESEM images of PUF/DCPD microcapsules illustrating (a) the uneven porous outer shell layer and (b) the surface of the smooth continuous inner shell wall on which precipitations of PUF nanobeads are adhered	70
Figure 3-12	FESEM micrographs of ruptured PUF microcapsule shell showing (a) the rough porous outer shell layer and (b) the smooth continuous inner shell	71
Figure 3-13	TGA diagram of PUF/DCPD microcapsules	72
Figure 3-14	FTIR spectra of (a) the extracted PUF capsule shell material, (b) PUF/DCPD microcapsules in the size range of 300-500 microns, and (c) PUF/DCPD microcapsules of 150-300 microns diameters, in comparison with the spectrum of the neat DCPD	75
Figure 3-15	FTIR-ATR spectra of (a) extracted PUF shell material, (b) PUF/DCPD microcapsules and (c) pure DCPD	77
Figure 3-16	DSC plots of PUF/DCPD microcapsules and extracted PUF microcapsule shell material	78
Figure 3-17	Proton NMR spectrum in acetone of the extracted core monomer of the PUF/DCPD microcapsules	79
Figure 3-18	(a) Digital micrograph showing PUF/TEGDMA microcapsules and (b) optical micrograph illustrating PUF microcapsules that contain a 1:1 Bis-GMA/TEGDMA mixture	81
Figure 3-19	DSC curves of PUF/DCPD microcapsules after different storage times	84

Figure 4-1	FTIR-ATR spectra of extracted neat PUF capsule shell matter in comparison with the extracted melamine modified PUF shell material	95
Figure 4-2	DSC plots of extracted PUF microcapsule shell matter: (a) neat PUF material and (b) the shell material in which 5% of the urea were replaced with melamine	96
Figure 4-3	TGA curves of extracted PUF microcapsule shell material in comparison with the melamine modified shell material	97
Figure 4-4	Optical micrographs of (a) 3 wt% and (b) 6 wt% PUF/DCPD microcapsules embedded in a dental host material	99
Figure 4-5	FESEM images of (a) melamine modified PUF/DCPD microcapsule embedded in a dental host material, and (b) the interface of the microcapsule shell and the dental matrix material	100
Figure 4-6	Flexural Strength of dental polymeric materials containing PUF/DCPD microcapsules which comprise different melamine amounts in their shell. The dental materials incorporated (a) 3 wt% and (b) 6 wt% microcapsules	101
Figure 4-7	Vickers hardness of dental polymeric materials containing (a) 3 wt% PUF/DCPD microcapsules and (b) 6 wt% microcapsules with different melamine amounts in the PUF shell	103
Figure 4-8	Nanoindentation hardness of dental polymeric materials containing (a) 3 wt% PUF/DCPD microcapsules and (b) 6 wt% PUF/DCPD microcapsules with different melamine amounts in the capsule shell	104

Figure 4-9	Young's Modulus obtained from nanoindentation hardness measurements of dental polymeric materials containing (a) 3 wt% PUF/DCPD microcapsules and (b) 6 wt% PUF/DCPD microcapsules with different melamine amounts in the microcapsule shell	106
Figure 5-1	Comparison of two microencapsulation procedures utilizing (a) the acid-catalysed <i>in situ</i> condensation polymerization of urea with formaldehyde to form the microcapsule wall in a single-step procedure and (b) the two-step encapsulation procedure	112
Figure 5-2	(a) Digital micrograph of PUF/epoxy microcapsules and (b) optical micrograph of the same capsules revealing their irregular shape	121
Figure 5-3	FESEM images illustrating (a) PUF/epoxy microcapsules and (b) the capsule surface on which individual spherical nanoparticles are attached	122
Figure 5-4	¹ H-NMR spectrum of the extracted ground PUF/epoxy microcapsules showing the characteristic peaks of the encapsulated epoxy resins DGEBA and BGE	123
Figure 5-5	DSC curves representing the heat flow of PUF/epoxy microcapsules in comparison with the extracted PUF shell matter	124

Figure 5-6	FESEM images of (a) PUF microcapsule containing Epikote 828/BGE embedded in an epoxy-based matrix material and (b) the interface of the microcapsule shell and the epoxy host material	126
Figure A1	Area of FESEM-EDX measurement on smooth microcapsule shell surface	151
Figure A2	FESEM-EDX spectra obtained from elemental analysis of the smooth microcapsule shell surface	152
Figure A3	Area of FESEM-EDX measurement on outer microcapsule shell layer	153
Figure A4	FESEM-EDX spectra obtained from elemental analysis of the outer microcapsule shell layer	154
Figure B1	TGA traces of PUF/DCPD microcapsules after ageing	155

LIST OF TABLES

		Page
Table 2-1	Stages during the chain reaction process of a free radical addition polymerization	12
Table 2-2	Comparison of relevant properties of selected acrylic dental monomers	14
Table 2-3	Volume shrinkage upon polymerization of selected acrylate-based direct restorative composite materials	16
Table 2-4	Examples of three different types of epoxy curing agents and their properties	20
Table 2-5	Different important microencapsulation techniques	30
Table 2-6	Examples of possible particle sizes that can be produced by certain specific encapsulation techniques	30
Table 2-7	Common methods for the determination of indentation hardness	42
Table 3-1	Varying urea and formaldehyde amounts for the preparation of PUF/DCPD microcapsules	52
Table 3-2	Total yield and yield according to different size fractions of PUF/DCPD microcapsules	67
Table 3-3	Composition of the smooth inner membrane and the rough porous outer layer of the microcapsule shell obtained from FESEM-EDX analysis	70

Table 4-1	Urea and melamine parts used for the preparation of the melamine modified PUF/DCPD microcapsule test series	88
Table 5-1	Variations of parameters and ingredients during the course of the encapsulation trials of epoxy resin in a PUF shell following the two-step microencapsulation method	112
Table 5-2	Epoxy resin mixtures for the encapsulation in a PUF shell following the single-step microencapsulation method	114
Table 5-3	Description and properties of different types of fumed silica available under the trade name ‘Aerosil’ (Evonik-Degussa)	116
Table 5-4	Proportions of selected curing agents to be used with Epikote 828 as recommended by the supplier	119
Table A1	Standard Measurement FESEM-EDX	152
Table A2	Composition of smooth microcapsule shell; elemental analysis by FESEM-EDX	152
Table A3	Composition of outer microcapsule shell layer; elemental analysis by FESEM-EDX	154
Table C1	Flexural strength of dental resin material incorporating 3% microcapsules with different melamine amounts in the capsule shell; reference: without capsules	156
Table C2	Flexural strength of dental resin material incorporating 6% microcapsules with different melamine amounts in the capsule shell; reference: without capsules	157

Table C3	Vickers hardness test results of neat dental resin material	158
Table C4	Vickers hardness test results of dental resin material incorporating 6% PUF/DCPD microcapsules	158
Table C5	Vickers hardness test results of dental resin material incorporating 6% microcapsules with 0.5% of the urea part in the capsule shell replaced by melamine	159
Table C6	Vickers hardness test results of dental resin material incorporating 6% microcapsules with 1% of the urea part in the capsule shell replaced by melamine	159
Table C7	Vickers hardness test results of dental resin material incorporating 6% microcapsules with 2% of the urea part in the capsule shell replaced by melamine	159
Table C8	Vickers hardness test results of dental resin material incorporating 6% microcapsules with 3% of the urea part in the capsule shell replaced by melamine	160
Table C9	Vickers hardness test results of dental resin material incorporating 6% microcapsules with 4% of the urea part in the capsule shell replaced by melamine	160
Table C10	Vickers hardness test results of dental resin material incorporating 6% microcapsules with 5% of the urea part in the capsule shell replaced by melamine	160
Table C11	Vickers hardness test results of dental resin material incorporating 3% PUF/DCPD microcapsules (reference, without melamine modification)	161

Table C12	Vickers hardness test results of dental resin material incorporating 3% microcapsules with 1% of the urea part in the capsule shell replaced by melamine	161
Table C13	Vickers hardness test results of dental resin material incorporating 3% microcapsules with 3% of the urea part in the capsule shell replaced by melamine	161
Table C14	Vickers hardness test results of dental resin material incorporating 3% microcapsules with 5% of the urea part in the capsule shell replaced by melamine	162
Table C15	Nanoindentation hardness of dental resin material incorporating 3% microcapsules with part of the urea in the capsule shell being replaced by melamine	164
Table C16	Indentation modulus of dental resin material incorporating 3% microcapsules with part of the urea in the capsule shell being replaced by melamine	164
Table C17	Nanoindentation hardness of dental resin material incorporating 6% microcapsules in which part of the urea in the capsule shell was replaced by melamine	165
Table C18	Indentation modulus of dental resin material incorporating 6% microcapsules in which part of the urea in the capsule shell was replaced by melamine	166

LIST OF ABBREVIATIONS

ADA	American Dental Association
ANSI	American National Standards Institute
ATR	Attenuated total reflectance
BADGE	Bisphenol A diglycidylether
BET	Specific surface area (Brunauer Emmett Teller)
BGE	Butyl glycidyl ether / 1-Butoxy-2,3-epoxypropane
Bis-GMA	Bisphenylglycidyl-dimethacrylate / 2,2-Bis-[4-(2-hydroxy-3-methacryloyloxypropoxyphenyl)]propane
BP	Benzoyl peroxide
CQ	Camphorquinone
DCPD	Dicyclopentadiene / 3a,4,7,7a-tetrahydro-4,7-methano-1H-indene
DETA	Diethylene triamine
DGEBA	Diglycidylether of bisphenol A / 2-[[4-[2-[4-(oxiran-2-ylmethoxy)phenyl]propan-2-yl]phenoxy]methyl]oxirane
DSC	Differential scanning calorimetry
ECHM-ECHC	3,4-Epoxy cyclohexylmethyl-3,4-epoxycyclohexane carboxylate
EDMAB	Ethyl-p-dimethylaminobenzoate
EDX	Energy-dispersive X-ray
EMA	Ethylene maleic anhydride
FESEM	Field emission gun scanning electron microscopy

FTIR	Fourier transform infrared
HV	Vickers Hardness
ISO	International Standard Organization
KBr	Potassium bromide
MF	Melamine-formaldehyde
MMA	Methyl methacrylate
MUF	Melamine-urea-formaldehyde
MW	Molecular weight
NMR	Nuclear magnetic resonance
OM	Optical microscopy
OOP	Out of plane
PU, PUR	Polyurethane
PUF	Poly(urea-formaldehyde)
ROMP	Ring-opening metathesis polymerization
ROP	Ring-opening polymerization
SDBS	Sodium dodecylbenzene sulphonate
SEM	Scanning electron microscopy
SI	International System of Units
TEA	Triethanolamine
TEGDMA	Tri(ethyleneglycol)dimethacrylate
UDMA	Urethane-dimethacrylat / 1,6-bis-(methacryloyloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane
UF	Urea-formaldehyde
UMF	Urea-melamine-formaldehyde
UMH	Ultra micro hardness

LIST OF SYMBOLS AND UNITS

ΔH	Enthalpy of transition
ΔH_m	Enthalpy of melting
gf	Gramm force
kp	Kilopond
phr	Parts per hundred parts
R	Alkyl group
R·	Free radical
T_g	Glass transition temperature
T_m	Melting temperature