SELF-HEALING POLYMERIC MATERIALS FOR POTENTIAL DENTAL APPLICATION

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THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2011

UNIVERSITI MALAYA

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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 ^{1}H-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 ^{1}H-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 ^{1}H-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 mempertingkat 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-butil 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.

ACKNOWLEDGEMENTS

This study would not have been possible without the help and assistance of many. First and foremost, I would like to express my sincere gratitude to my supervisor, Professor Dr. Gan Seng Neon for his invaluable time and inspiring guidance throughout the course of this work. I also gratefully acknowledge the time, support and enthusiasm from my co-supervisor, Professor Dr. Noor Hayaty Abu Kasim. It has been a great learning experience and opportunity to work with the two of you.

Special thanks to my friend Hamid Khaledi for his encouragement, advice, cordial discussions and intellectual contributions. Thanks for being there to cheer me up whenever I would get discouraged.

I extend my thanks to all my lovely lab colleagues, especially Shafizah and Siang Yin. It has been a pleasure working with you! Thanks are also due to the staff of the Chemistry Department and the Department of Conservative Dentistry for their cooperation and help. In particular, I would like to recognize Miss Ho and Encik Zol from the polymer teaching lab, Professor Dr. Misni Misran and his research students for their assistance in using the instruments in their laboratory, and Professor Rosiyah Yahya for her fruitful discussions. Many thanks also to Puan Zarina and Dr. Fadhel Alsanabani who always provided help during my work in the 'Makmal Biobahan', Encik Zaini for his joy at fabricating mechanical test moulds according to my specific needs, and the personnel of the Combinatorial Technology and Catalysis Research Center (COMBICAT). I was fortunate to work in a truly interdisciplinary environment which greatly enhanced my research experience.

This work was made possible with the research grants provided from the University of Malaya and the project funding from the Ministry of Science, Technology and Innovation (MOSTI, 03-01-03-SF0550). I am truly grateful for their support. Furthermore, I greatly acknowledge the financial aid from the company Nestle (Malaysia) Berhard and my friend Ingo Waessle who supported me in so many ways. Thanks for bringing me to this beautiful country and giving me the unique chance to study here and experience the people and the customs of Malays, Chinese, and Indians.

Last but not least, I am thanking all my friends for their support, especially my sister Sabine, my friend Annette and Heidi who I challenged with managing my affairs at home during my absence.

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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-[4-92-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-Epoxycyclohexylmethyl-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