

# CONTENTS

	Page
<b>ACKNOWLEDGEMENTS</b>	iii
<b>ABSTRACT (English)</b>	iv
<b>ABSTRACT (Thai)</b>	vi
<b>LIST OF TABLES</b>	xiv
<b>LIST OF FIGURES</b>	xix
<b>ABBREVIATIONS</b>	xxii
<b>CHAPTER 1</b>	
<b>INTRODUCTION</b>	
1.1 Structure of the Skin	1
1.1.1 Epidermis	1
1.1.2 Dermis	4
1.1.3 Subcutaneous Tissue	7
1.2 Functions of the Skin	7
1.3 Burns and Other Thermal Injuries	10
1.4 Classification of Burns	11
1.5 Requirements of Temporary Skin Substitutes Used as Burn Dressings	13
1.6 Rationale and Aims of this Study	16

**CHAPTER 2****BIOMEDICAL APPLICATIONS OF  
SYNTHETIC HYDROGELS**

2.1	Introduction	19
2.2	Definitions of Hydrogels	20
2.3	Hydrogels Based on Hydroxyalkyl Methacrylate	21
2.4	The Hydrogel - Water Interface	22
2.5	Factors Affecting the Swelling of Hydrogels	24
2.6	Synthesis and Fabrication of Hydrogels	26
2.7	Perceived Advantages of Hydrogels as Biomaterials	34
2.8	Application of Synthetic Hydrogels as Wound Dressings	35

**CHAPTER 3****EXPERIMENTAL METHODS AND RESULTS**

3.1	Chemicals, Apparatus and Instruments	40
	3.1.1 Chemicals	40
	3.1.2 Apparatus and Instruments	41
3.2	Purifications and Analyses of Initiator, Crosslinking Agent and Monomers	42
	3.2.1 Recrystallisation of Initiator	42
	3.2.2 Vacuum Distillation of Crosslinking Agent	44

	Page
3.2.3 Distillation of Monomers	47
3.2.3.1 2-Hydroxyethyl Methacrylate	47
3.2.3.2 Butyl Acrylate	50
3.2.3.3 Methyl Acrylate	51
3.3 Bulk Polymerisation in the Form of Thin Sheets	54
3.3.1 Mound Design	54
3.3.2 Bulk Polymerisation / Copolymerisation Procedure	55
3.4 Polymer Characterisation	57
3.4.1 Polymer Properties Relevant to Intended Application	57
3.4.2 Solubility	59
3.4.3 Infrared Spectroscopy	62
3.4.4 Elemental Analysis	71
3.5 Thermal Analysis	75
3.5.1 Differential Scanning Calorimetry	75
3.5.2 Thermogravimetry	85
3.6 Water Absorption and Retention Properties	91
3.6.1 Water Absorption and Equilibrium Water Content	91
3.6.2 Water Retention	100
3.7 Water Vapour Transmission	111
3.7.1 Inverted Cup Method : Test Procedure	113
3.8 Mechanical Properties	132
3.8.1 Definitions of Terms Relating to Tensile Testing	133
3.8.2 Tensile Test Procedure	137

**CHAPTER 4****DISCUSSION AND CONCLUSIONS**

4.1	Hydrogel Synthesis	149
4.2	The Nature of Hydrogel-Water Interactions	152
4.3	Glass Transition Temperature	156
4.4	Thermal Stability	157
4.5	Water Absorption and Retention Properties	160
4.6	Water Vapour Transmission Properties	164
4.7	Mechanical Properties	168
4.8	Overall Conclusion	172
	<b>SUGGESTIONS FOR FURTHER WORK</b>	174
	<b>REFERENCES</b>	176
	<b>APPENDIX</b>	181
	<b>VITA</b>	186

## LIST OF TABLES

Table	Page	
1.1	Descriptions of the various burn ratings by degree	13
2.1	Factors that influence the swelling of hydrogels	24
2.2	Monomers used in hydrogel preparation	27
2.3	Converted polymers used as hydrogels	29
2.4	A brief list of the biomedical applications of synthetic hydrogels	33
3.1	Chemicals used in this research	40
3.2	Apparatus and instruments used in this research	41
3.3	Infrared absorption band assignments for recrystallised benzoyl peroxide	44
3.4	Infrared absorption band assignments for the distilled ethylene glycol dimethacrylate crosslinking agent	46
3.5	Infrared absorption band assignments for the distilled 2-hydroxyethyl methacrylate monomer	49
3.6	Infrared absorption band assignments for the distilled butyl acrylate monomer	51
3.7	Infrared absorption band assignments for methyl acrylate monomer	54
3.8	Comonomer feed compositions of HEMA and BA used in copolymer synthesis	56
3.9	Comonomer feed compositions of HEMA and MA used in copolymer synthesis	57

Table	Page
3.10 Some properties of the dry polymer or copolymer sheets relevant to their use as temporary skin substitutes	58
3.11 Some properties of the hydrated polymer or copolymer sheets relevant to their use as temporary skin substitutes	59
3.12 Solubility test results for the uncrosslinked homopolymers	61
3.13 Infrared absorption band assignments for crosslinked P(HEMA)	62
3.14 Infrared absorption band assignments for crosslinked PBA	66
3.15 Infrared absorption band assignments for crosslinked PMA	66
3.16 Elemental analysis results for the homopolymers	73
3.17 Elemental analysis results for the crosslinked copolymers	74
3.18 Comparison of the glass transition temperatures, $T_g$ , obtained from the DSC curves of the homopolymers and copolymers	84
3.19 Thermal degradation characteristics of the homopolymers and copolymers	90
3.20 Increasing water contents of the P(HEMA) homopolymers immersed in deionized water for different times at 35°C	93
3.21 Increasing water contents of the PBA homopolymers immersed in deionized water for different times at 35°C	94
3.22 Increasing water contents of the PMA homopolymers immersed in deionized water for different times at 35°C	95
3.23 Increasing water contents of the crosslinked P(HEMA-co-BA) copolymers immersed in deionized water for different times at 35°C	97

Table	Page
3.24 Increasing water contents of the crosslinked P(HEMA-co-MA) copolymers immersed in deionized water for different times at 35°C	98
3.25 Water retentions of the P(HEMA) homopolymers as a function of time	101
3.26 Water retentions of the PBA homopolymers as a function of time	102
3.27 Water retentions of the PMA homopolymers as a function of time	103
3.28 Water retentions of the crosslinked P(HEMA-co-BA) copolymers as a function of time	106
3.29 Water retentions of the crosslinked P(HEMA-co-MA) copolymers as a function of time	107
3.30 Comparison of equilibrium water contents (EWC) of the hydrogels studied in both water and air	110
3.31 Water vapour transmission test results for uncrosslinked P(HEMA)	116
3.32 Water vapour transmission test results for crosslinked P(HEMA)	118
3.33 Water vapour transmission test results for uncrosslinked PBA	119
3.34 Water vapour transmission test results for crosslinked PBA	120
3.35 Water vapour transmission test results for uncrosslinked PMA	121
3.36 Water vapour transmission test results for crosslinked PMA	122
3.37 Water vapour transmission test results for crosslinked P(HEMA-co-BA) / 95:5 copolymer	123

Table	Page
3.38 Water vapour transmission test results for crosslinked P(HEMA-co-BA) / 90:10 copolymer	124
3.39 Water vapour transmission test results for crosslinked P(HEMA-co-BA) / 85:15 copolymer	125
3.40 Water vapour transmission test results for crosslinked P(HEMA-co-BA) / 80:20 copolymer	126
3.41 Water vapour transmission test results for crosslinked P(HEMA-co-MA) / 95:5 copolymer	127
3.42 Water vapour transmission test results for crosslinked P(HEMA-co-MA) / 90:10 copolymer	128
3.43 Water vapour transmission test results for crosslinked P(HEMA-co-MA) / 85:15 copolymer	129
3.44 Water vapour transmission test results for crosslinked P(HEMA-co-MA) / 80:20 copolymer	130
3.45 Comparison of the WVT rates for all of the homopolymers and copolymers studied in this work : 'Inverted cup' method	131
3.46 Mechanical property test results for the hydrated uncrosslinked P(HEMA) homopolymer (EWC $\approx$ 37.3%)	140
3.47 Mechanical property test results for the hydrated crosslinked P(HEMA) homopolymer (EWC $\approx$ 33.7%)	140
3.48 Mechanical property test results for the uncrosslinked PBA homopolymer (EWC = 1.36%)	141
3.49 Mechanical property test results for the crosslinked PBA homopolymer (EWC = 0.87%)	141



Table	Page
3.50 Mechanical property test results for the uncrosslinked PMA homopolymer (EWC = 3.13%)	142
3.51 Mechanical property test results for the crosslinked PMA homopolymer (EWC = 2.11%)	142
3.52 Mechanical property test results for the hydrated crosslinked P(HEMA-co-BA) / 95:5 copolymer (EWC = 30.2%)	143
3.53 Mechanical property test results for the hydrated crosslinked P(HEMA-co-BA) / 90:10 copolymer (EWC = 27.4%)	143
3.54 Mechanical property test results for the hydrated crosslinked P(HEMA-co-BA) / 85:15 copolymer (EWC = 25.7%)	144
3.55 Mechanical property test results for the hydrated crosslinked P(HEMA-co-BA) / 80:20 copolymer (EWC = 22.3%)	144
3.56 Mechanical property test results for the hydrated crosslinked P(HEMA-co-MA) / 95:5 copolymer (EWC = 34.0%)	145
3.57 Mechanical property test results for the hydrated crosslinked P(HEMA-co-MA) / 90:10 copolymer (EWC = 32.8%)	145
3.58 Mechanical property test results for the hydrated crosslinked P(HEMA-co-MA) / 85:15 copolymer (EWC = 31.8%)	146
3.59 Mechanical property test results for the hydrated crosslinked P(HEMA-co-MA) / 80:20 copolymer (EWC = 30.5%)	146
3.60 Comparison of the (average) mechanical property values for the hydrated homopolymers and copolymers	148

Table	Page
4.1 Water vapour transmission (WVT) rates and surface temperatures reported by Lamke et al.	165
4.2 Summary of the mechanical properties of the hydrogel samples prepared in this work, each tested in its equilibrium hydrated state	169

## LIST OF FIGURES

Figure	Page
1.1 A sectional view of typical skin	3
1.2 Micrographs of skin	6
1.3 A reconstruction of a block of skin	9
1.4 Layers of the skin showing the comparative depths of first, second, and third-degree burns	12
2.1 Schematic representation of the hydrogel-water interface	23
2.2 Water entrance into a single, idealized hydrogel chain segment	26
2.3 Fabrication of hydrogels	31
3.1 Infrared spectrum of recrystallized benzoyl peroxide	43
3.2 Reference infrared spectrum of benzoyl peroxide	43
3.3 Vacuum distillation apparatus used in the purification of the ethylene glycol dimethacrylate crosslinking agent	45
3.4 Infrared spectrum of distilled ethylene glycol dimethacrylate	45
3.5 Reference infrared spectrum of ethylene glycol dimethacrylate	46
3.6 Infrared spectrum of distilled 2-hydroxyethyl methacrylate	48
3.7 Reference infrared spectrum of 2-hydroxyethyl methacrylate	48
3.8 Infrared spectrum of distilled butyl acrylate	50
3.9 Simple distillation apparatus used in the purification of methyl acrylate monomer	52
3.10 Infrared spectrum of distilled methyl acrylate	53
3.11 Reference infrared spectrum of methyl acrylate	53
3.12 Mould used for bulk polymerisation in the form of thin sheets	55
3.13 Infrared spectrum of crosslinked P(HEMA)	63

Figure	Page
3.14 Reference infrared spectrum of P(HEMA)	63
3.15 Infrared spectrum of crosslinked PBA	64
3.16 Reference infrared spectrum of PBA	64
3.17 Infrared spectrum of crosslinked PMA	65
3.18 Reference infrared spectrum of PMA	65
3.19 Infrared spectrum of crosslinked P(HEMA-co-BA)/95:5	67
3.20 Infrared spectrum of crosslinked P(HEMA-co-BA)/90:10	67
3.21 Infrared spectrum of crosslinked P(HEMA-co-BA)/85:15	68
3.22 Infrared spectrum of crosslinked P(HEMA-co-BA)/80:20	68
3.23 Infrared spectrum of crosslinked P(HEMA-co-MA)/95:5	69
3.24 Infrared spectrum of crosslinked P(HEMA-co-MA)/90:10	69
3.25 Infrared spectrum of crosslinked P(HEMA-co-MA)/85:15	70
3.26 Infrared spectrum of crosslinked P(HEMA-co-MA)/80:20	70
3.27 DSC thermogram of uncrosslinked P(HEMA)	76
3.28 DSC thermogram of crosslinked P(HEMA)	77
3.29 DSC thermogram of uncrosslinked PBA	77
3.30 DSC thermogram of crosslinked PBA	78
3.31 DSC thermogram of uncrosslinked PMA	78
3.32 DSC thermogram of crosslinked PMA	79
3.33 DSC thermogram of crosslinked P(HEMA-co-BA)/95:5	79
3.34 DSC thermogram of crosslinked P(HEMA-co-BA)/90:10	80
3.35 DSC thermogram of crosslinked P(HEMA-co-BA)/85:15	80
3.36 DSC thermogram of crosslinked P(HEMA-co-BA)/80:20	81
3.37 DSC thermogram of crosslinked P(HEMA-co-MA)/95:5	81

Figure	Page
3.38 DSC thermogram of crosslinked P(HEMA-co-MA)/90:10	82
3.39 DSC thermogram of crosslinked P(HEMA-co-MA)/85:15	82
3.40 DSC thermogram of crosslinked P(HEMA-co-MA)/80:20	83
3.41 Dynamic TG thermogram and 1st derivative curve of uncrosslinked P(HEMA)	86
3.42 Dynamic TG thermogram and 1st derivative curve of crosslinked P(HEMA)	86
3.43 Dynamic TG thermogram and 1st derivative curve of uncrosslinked PBA	87
3.44 Dynamic TG thermogram and 1st derivative curve of crosslinked PBA	87
3.45 Dynamic TG thermogram and 1st derivative curve of uncrosslinked PMA	88
3.46 Dynamic TG thermogram and 1st derivative curve of crosslinked PMA	88
3.47 Dynamic TG thermograms and of the crosslinked P(HEMA-co-BA) copolymers	89
3.48 Dynamic TG thermograms and of the crosslinked P(HEMA-co-MA) copolymers	89
3.49 Water content - time profiles for P(HEMA) in deionized water at 35°C showing the effect of crosslinking	96

Figure	Page
3.50 Water content - time profiles for PBA and PMA in deionized water at 35°C showing the effect of crosslinking and chemical structure	96
3.51 Water content - time profiles for crosslinked P(HEMA-co-BA) in deionized water at 35°C showing the effect of copolymer composition	99
3.52 Water content - time profiles for crosslinked P(HEMA-co-MA) in deionized water at 35°C showing the effect of copolymer composition	99
3.53 Time dependence of the water retentions of the uncrosslinked and crosslinked P(HEMA) hydrogels in air at 35.0°C	104
3.54 Time dependence of the water retentions of the uncrosslinked and crosslinked PBA hydrogels in air at 35.0°C	104
3.55 Time dependence of the water retentions of the uncrosslinked and crosslinked PMA hydrogels in air at 35.0°C	105
3.56 Effect of copolymer composition on the water retention of crosslinked P(HEMA-co-BA) in air at 35.0°C	108
3.57 Effect of copolymer composition on the water retention of crosslinked P(HEMA-co-MA) in air at 35.0°C	108
3.58 Expanded view of the aluminium cup assembly used for water vapour transmission (WVT) measurements	112
3.59 Internal arrangement employed inside the incubator for the “Inverted Cup” method of WVT determination	114
3.60 WVT plot for the uncrosslinked P(HEMA) hydrogel	117

Figure	Page
3.61 Typical stress-strain curve for thermoplastic materials	135
3.62 Different types of stress-strain curves	136
3.63 Tensile stress-strain curve designations	137
3.64 Stress-strain curves of the uncrosslinked P(HEMA) homopolymer	139
3.65 Stress-strain curves of the crosslinked PMA homopolymer	139
4.1 Structural representation of P(HEMA) crosslinked by EGDMA	150
4.2 Different levels of polymer-water interaction in P(HEMA)	153
4.3 DSC thermogram of hydrated P(HEMA) hydrogel showing the water volatilisation endotherm	155
4.4 DSC thermogram of distilled water alone showing the volatilisation endotherm	155
4.5 Effect of copolymer composition on the EWC of the P(HEMA-co-BA) and P(HEMA-co-MA) hydrogels when immersed in deionized water at 35.0°C	162
4.6 Effect of copolymer composition on the EWC retained by the P(HEMA-co-BA) and P(HEMA-co-MA) hydrogels when left in air at 35.0°C	162
4.7 Effect of copolymer composition on the water vapour transmission (WVT) rates of the P(HEMA-co-BA) and P(HEMA-co-MA) hydrogels	167

## ABBREVIATIONS

cm	centrimetre
HEMA	2-hydroxyethyl methacrylate
BA	butyl acrylate
MA	methyl acrylate
IPN	interpenetrating polymer network
EGDMA	ethylene glycol dimethacrylate
P(HEMA)	poly(2-hydroxyethyl methacrylate)
PBA	poly(butyl acrylate)
PMA	poly(methyl acrylate)
P(HEMA-co-BA)	poly(2-hydroxyethyl methacrylate-co-butyl acrylate)
P(HEMA-co-MA)	poly(2-hydroxyethyl methacrylate-co-methyl acrylate)
DSC	differential scanning calorimetry
TG	thermogravimetry
FT-IR	Fourier transform infrared spectrometry
°C	degree Celcius
mg	milligram
min	minute
T <sub>g</sub>	glass transition temperature
IPT	inflection point temperature
WC	water content
EWC	equilibrium water content
WVT	water vapour transmission