

TABLE OF CONTENTS

ABSTRAK.....	i
ABSTRACT.....	iv
ACKNOWLEDGEMENTS.....	vii
CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW.....	1
1.1 Introduction.....	1
1.2 Types of coatings.....	5
1.2.1 High-solid coatings (Solvent borne).....	5
1.2.2 Water borne coatings.....	7
1.2.3 Powder coatings.....	9
1.3 Chemistry of alkyd resins.....	11
1.3.1 Raw material selection.....	11
1.3.2 Fatty acids and Oil.....	11
1.3.3 Polyols.....	15
1.3.4 Polybasic acids.....	18
1.4 Classification of alkyd resins.....	21
1.5 Synthesis of alkyd resin.....	24
1.5.1 Monoglyceride process (Alcoholysis).....	24
1.5.2 Fatty acid process.....	25
1.6 Process variations.....	27
1.7 Estimation of progress of reaction.....	29
1.8 Classification of polymers by the kinetic mechanism.....	30
1.8.1 Free radical polymerization.....	30
1.8.2 Step growth polymerization.....	33
1.9 Monomer selection.....	34
1.10 Alkyd based coatings.....	35

1.11	Scopes of study.....	42
CHAPTER 2: EXPERIMENTAL.....		44
2.1	Materials.....	44
2.2	Procedure of macromers synthesis.....	44
2.2.1	Procedure of determination of acid number.....	46
2.2.2	Standardization of potassium hydroxide.....	47
2.2.3	Sample and blank titration.....	47
2.2.4	Procedure of determination of hydroxyl number.....	48
2.2.5	Preparation of test reagents.....	48
2.2.6	Titration of sample and blank.....	49
2.3	Preparation of macromer-methyl methacrylate copolymers (MMC).....	51
2.4	The modification of copolymers using butyl acrylate (BA) monomer (MMBC).....	52
2.5	Conversion (%) of polymerization.....	53
2.6	Solid content.....	54
2.7	Solvent extraction.....	54
2.8	Swelling test.....	55
2.9	Characterization methods.....	55
2.9.1	Fourier Transform Infrared analysis (FTIR).....	55
2.9.2	Nuclear Magnetic Resonance (¹ H-NMR and ¹³ C-NMR).....	56
2.9.3	Differential Scanning Calorimetry (DSC).....	56
2.9.4	Thermogravimetry analysis (TGA).....	58
2.9.5	Gel-permeation chromatography (GPC).....	59
2.9.6	Dynamic mechanical analysis (DMA).....	60
CHAPTER 3: RESULTS AND DISCUSSION.....		62
3.1	Synthesis of AlkOA65.....	63
3.2	Synthesis of AlkOA40.....	65

3.3	Synthesis of AlkOA28.....	65
3.4	Reduction of the acid number during the preparation of macromer.....	66
3.4.1	Calculation of extent of reaction and average degree of polymerization based on acid number.....	71
3.5	Characterization of synthesized macromers.....	74
3.5.1	Hydroxyl number determination of macromers.....	75
3.5.2	FTIR spectroscopy.....	78
3.5.3	¹ H-NMR spectroscopy.....	79
3.5.4	¹³ C-NMR Spectroscopy.....	80
3.5.5	Gel-permeation chromatography (GPC).....	82
3.5.6	Differential Scanning Calorimetry (DSC analysis).....	82
3.5.7	Thermogravimetric analysis (TGA).....	83
3.6	Summary.....	97

CHAPTER 4: COPOLYMERIZATION OF PALM OLEIC ACID-BASED MACROMERS WITH METHYL METHACRYLATE AND BUTYL ACRYLATE.....98

4.1	Preparation of macromer-methyl methacrylate copolymers (MMC).....	98
4.1.1	Effect of macromer content on the conversion (%).	98
4.2	Evidence on formation of true copolymer.....	102
4.2.1	FTIR spectroscopy.....	102
4.2.2	¹ H-NMR Spectroscopy.....	104
4.2.3	Solvent extraction.....	106
4.3	Percentage of swelling in toluene for MMC copolymers.....	107
4.4	Molecular weight distributions.....	108
4.5	Thermal analysis.....	109
4.5.1	DSC analysis.....	109
4.5.2	Thermogravimetry Analysis (TGA).....	112
4.6	Dynamic mechanical analysis (DMA).....	115

4.6.1	Peak analysis of DMA.....	115
4.6.2	Glass transition temperature and mechanical properties of the copolymers (MMC) using DMA.....	117
4.7	Modification of synthesized copolymers (MMC) with BA monomer: effect of macromer content on conversion (%).	119
4.8	FTIR Spectroscopy of MMBC copolymers.....	124
4.9	¹ H-NMR Spectroscopy of MMBC copolymers.....	125
4.10	DSC analysis of MMBC copolymers.....	127
4.11	Percentage of swelling in toluene for MMBC copolymers.....	128
4.12	GPC results of MMBC copolymers.....	128
4.13	Thermogravimetry Analysis (TGA) of MMBC copolymers.....	129
4.14	Glass transition temperature and mechanical properties of MMBC copolymers using DMA.....	134
4.15	Summary.....	136

CHAPTER 5: CHARACTERIZATION OF COPOLYMERS AS COATING MATERIALS.

	137
5.1	Preparation on mild steel panels and coating application.....	138
5.2	Tests on coatings properties.....	139
5.2.1	Solid ontent.....	139
5.2.2	Drying time test.....	140
5.2.3	Adhesion measurement.....	141
5.2.4	Pencil hardness test.....	142
5.2.5	Water immersion testing.....	143
5.2.6	Acid resistance test.....	144
5.2.7	Alkali resistance test.....	144
5.2.8	Salt water resistance test.....	144

5.2.9 Solvent resistance test (Solvent rub).....	145
5.3 Results and discussion.....	146
5.3.1 Coatings appearance.....	146
5.3.2 Drying time test.....	147
5.3.3 Adhesion measurement of methacrylate copolymers (MMC).....	148
5.3.4 Pencil hardness test.....	149
5.3.5 Water resistance.....	150
5.3.6 Acid, alkali and salt resistances.....	151
5.3.7 Solvent rub test.....	153
5.4 Effect of butyl acrylate monomer on coatings properties of MMBC samples....	155
5.4.1 Coatings appearance.....	155
5.4.2 Solid content of MMBC samples.....	155
5.4.3 Drying times of MMBC samples.....	155
5.4.4 Adhesion measurement of MMBC samples.....	156
5.4.5 Pencil hardness test for MMBC samples.....	158
5.4.6 Water resistance for MMBC samples.....	158
5.4.7 Acid, alkali and salt resistances for MMBC samples.....	159
5.4.8 Solvent rub test for MMBC samples.....	160
5.5 Summary.....	162
CHAPTER 6: CONCLUSION AND SCOPE FOR FURTHER RESEARCH.....	164
6.1 Conclusion.....	164
6.2 Suggestions for further research.....	166

LIST OF FIGURES

Figure 1.1 : Analysis of paint consumption by market in 2007.....	3
Figure 1.2:Typical polyol structures with hindered β positions relative to OH group.....	18
Figure 1.3: Effect of oil length and degree of unsaturation (Iodine Value) on the properties... of alkyd resin.....	23
Figure 1.4: Preparation of alkyd resin by monoglyceride process.....	25
Figure 1.5: The esterification reaction for the alkyd preparation by dibasic acid anhydrides.....	28
Figure 1.6 : A typical structure of an acrylic monomer.....	34
Figure 1.7 : Typical structure of hydroperoxide.....	36
Figure 2.1 : Representation of set up used in polyesterification of macromers including reaction flask; Dean-Stark decanter; Condenser; Stirrer motor; Stainless steel rode of stirrer and Thermometer.	46
Figure 2.2 : Representation of apparatus set up for copolymerization of the macromer with MMA [(a) Oil bath; (b) reaction flask; (c) Dropping funnel; (d) Condenser; (e) Stirrer motor; (f) Stainless steel rod of stirrer; (g) Digital thermometer and (h)Nitrogen cylinder)]	51
Figure 2.3 : Simple diagram of DSC instrument.....	57
Figure 3.1 : plots of changes in acid number versus reaction time for macromers.....	69
Figure 3.2 : A plausible reaction mechanism in the polyesterification of the macromers ...	70
Figure 3.3 : Graphs of $(1 - P)^{-1}$ against time for the macromer samples.....	73
Figure 3.4 : Infrared spectra of the AlkOA macromers and oleic acid	78
Figure 3.5 : $^1\text{H-NMR}$ spectrum and one of the plausible molecular structures of AlkOA40 80	
Figure 3.6 : $^{13}\text{C-NMR}$ Spectra for oleic acid (a) and macromer AlkOA65 (b).....	81
Figure 3.7 : TG (a) and DTG (b) curves of three macromers at heating rate $10^\circ\text{C}/\text{min}$	84
Figure 3.8 : TG (a) and DTG (b) thermograms of AlkOA28 at various heating rates	85
Figure 3.9 : TG (a) and DTG (b) thermograms of AlkOA40 at various heating rates	86

Figure 3.10 : TG (a) and DTG (b) thermograms of AlkOA65 at various heating rates	86
Figure 3.11 : Determination of E_d by Kissinger method for the three macromers	88
Figure 3.12 : Ozawa plots of AlkOA28 at various conversion of reaction: $\alpha = 0.1(\circ)$, $\alpha = 0.2(-)$, $\alpha = 0.3 (+)$, $\alpha = 0.4 (\blacklozenge)$, $\alpha = 0.5 (\lozenge)$, $\alpha = 0.6 (\times)$, $\alpha = 0.7 (\blacktriangle)$, $\alpha = 0.8 (\square)$, $\alpha = 0.9 (\bullet)$	92
Figure 3.13 : Activation energies corresponding to fixed values of α using Ozawa plots of AlkOA28.....	93
Figure 3.14 : Ozawa plots of AlkOA40 at various conversion of reaction: $\alpha = 0.1(\circ)$, $\alpha = 0.2(-)$, $\alpha = 0.3 (+)$, $\alpha = 0.4 (\blacklozenge)$, $\alpha = 0.5 (\lozenge)$, $\alpha = 0.6 (\times)$, $\alpha = 0.7 (\blacktriangle)$, $\alpha = 0.8 (\square)$, $\alpha = 0.9 (\bullet)$	94
Figure 3.15 : Activation energies corresponding to fixed values of α using Ozawa plots of AlkOA40.....	94
Figure 3.16 : Ozawa plots of AlkOA65 at various conversion of reaction: $\alpha = 0.1(\circ)$, $\alpha = 0.2(-)$, $\alpha = 0.3 (+)$, $\alpha = 0.4 (\blacklozenge)$, $\alpha = 0.5 (\lozenge)$, $\alpha = 0.6 (\times)$, $\alpha = 0.7 (\blacktriangle)$, $\alpha = 0.8 (\square)$, $\alpha = 0.9 (\bullet)$	96
Figure 3.17 : Activation energies corresponding to fixed values of α using Ozawa plots of.... AlkOA65.....	96
Figure 4.1 : Two plausible reaction mechanisms for the synthesis of the copolymers, proton abstraction (a), and addition mechanism to C=C (b).	99
Figure 4.2 : Conversion of copolymers of AL1, AL2 and AL3 with ratios 50%, 35% and 20% of AlkOA65 respectively	101
Figure 4.3 : Conversion of copolymers of AM1, AM2 and AM3 with ratios 50%, 35% and 20% of AlkOA40 respectively	101
Figure 4.4 : Conversion of copolymers of AS1, AS2 and AS3 with ratios 50%, 35% and 20% of AlkOA28 respectively	101
Figure 4.5 : Conversion (%) of PMMA and copolymers (MMC).....	102
Figure 4.6 : The FTIR spectra of AS copolymers, AlkOA28 macromer and PMMA	103
Figure 4.7 : $^1\text{H-NMR}$ spectra of oleic acid (A), AlkOA40 (B) and copolymer AM2 (C)...	105
Figure 4.8 : $^1\text{H-NMR}$ spectrum of copolymer AM2 after solvent extraction.....	107
Figure 4.9 : Chromatograms of AlkOA40, AM copolymers and PMMA	108
Figure 4.10: Overlay of DSC thermograms for the copolymers of AM series and PMMA	110
Figure 4.11 : The overlay TG thermograms AM series copolymers and PMMA.....	114

Figure 4.12 : Glass transition temperature as the maximum tan δ_{\max} and maximum E''_{\max}	116
Figure 4.13 : Two plausible reaction mechanisms for preparation MMBC copolymers....	120
Figure 4.14 : Conversion of modified copolymers with different ratios of AlkOA65/acrylate with 10 wt.% BA	122
Figure 4.15 : Conversion of modified copolymers with different ratios of AlkOA40/acrylate with 10 wt.% BA	122
Figure 4.16 : Conversion of modified copolymers with different ratios of AlkOA28/acrylate with 10 wt.% BA	122
Figure 4.17 : Conversion of modified copolymers with different ratios of AlkOA28/acrylate with 5 wt.% BA	123
Figure 4.18 : Conversion (%) MMBC copolymers.....	123
Figure 4.19 : Chemical structure of MMA	124
Figure 4.20 : Chemical structure of BA.....	124
Figure 4.21: FTIR spectra of AS1B(10%), AS2B(10%) and AS3B(10%) copolymers	125
Figure 4.22: ^1H NMR spectrum of AM2B and one of the plausible its molecular structure.....	126
Figure 4.23: Thermal stability of AlkOA65, AL2 and AL2B (a), AlkOA40, AM2 and AM2B (b), AlkOA28, AS2 and AS2B(10%) (c)	133
Figure 4.24 : Effect of different percentages of BA on thermal stability of modified copolymers of AS1	134
Figure 5.1 : Schematic diagram of a Sheen pencil hardness tester kit.....	143
Figure 5.2 : Coating performance: Coated panels of AS1 sample after one hour (a), after one year exposure in the open lab. bench (under hot and humid conditions) (b)	151
Figure 5.3 : Coated panel of AS3B(5%) sample after 8 months exposure in the open lab. bench (under hot and humid conditions)	159
Figure 5.4: Molecular structure of MMC samples and related reactive sites for chemical and mechanical.....	162

LIST OF TABLES

Table 1.1 : Some fatty acid compositions in natural oils	12
Table 1.2 : Some fatty acid distribution in several common natural oils (%)	13
Table 1.3 : World productions of oils and fats suitable as raw materials for oleochemicals (Million tones).	14
Table 1.4 : Some common polyalcohols used to synthesize of alkyd.....	16
Table 1.5 : Some common polybasic acids used to synthesize of alkyd	19
Table 1.6 : Characteristics of the alkyd synthesis procedure	27
Table 1.7 : Properties contributed by common acrylic monomers	35
Table 1.8 : Effect of side chain groups on polymer properties.....	35
Table 2.1 : Composition of oleic acid, PA and glycerol used in preparation of macromers .	45
Table 2.2 : Composition recipes and designation codes of the copolymers	52
Table 2.3 : Composition of modified copolymers using 5 wt.% and 10 wt.% BA	53
Table 3.1 : Theoretical calculation for the formulation of macromer AlkOA65	63
Table 3.2 : Formulation of AlkOA40.....	65
Table 3.3 : Formulation of AlkOA28.....	66
Table 3.4 : Titration results for standardization of alcoholic KOH	66
Table 3.5 : Titration results of AlkOA65 with standardized alcoholic KOH at 440 min	66
Table 3.6 : Variation of acid number with reaction time and \bar{X}_n during the synthesis of AlkOA65.....	67
Table 3.7 : Variation of acid number and \bar{X}_n during the synthesis of AlkOA40	68
Table 3.8 : Variation of acid number and \bar{X}_n during the synthesis of AlkOA28	68
Table 3.9 : Calculated P%, \bar{X}_n and k at the deviate point from linearity, and P% at the end of reaction for the macromers.....	73

Table 3.10 : Standardization of NaOH solution	76
Table 3.11 : Titration results of AlkOA65 with standardized NaOH solution.....	76
Table 3.12 : Titration results of AlkOA40 with standardized NaOH solution.....	76
Table 3.13 : Titration results of AlkOA28 with standardized NaOH solution.....	77
Table 3.14 : Hydroxyl and acid numbers of macromers.....	77
Table 3.15 : Major absorption peaks of macromers in FTIR spectra.....	79
Table 3.16 : Chemical shifts of ^{13}C -NMR spectra of oleic acid and macromer.....	82
Table 3.17: The molecular weight characteristics of macromers.....	82
Table 3.18: Glass transition temperatures of macromers.....	83
Table 3.19: E_d , A and k at different heating rates using Kissinger plots	87
Table 3.20 : Calculated E_d using the Ozawa method at various conversion using different heating rates for the three macromers.....	92
Table 4.1 : The absorption peaks of AS copolymers, AlkOA28 and PMMA	103
Table 4.2 : Chemical shifts of ^1H -NMR spectra of AlkOA40, AM2 and oleic acid	106
Table 4.3 : Swelling (%) in crosslinked copolymer of AS1	108
Table 4.4 : M_n , M_w and polydispersity of the copolymers (MMC) and PMMA based on GPC chromatograms	109
Table 4.5 : T_g (Expt.) and T_g (Cal.) of copolymers, T_g (Expt.) of PMMA	112
Table 4.6 : Thermal behaviour of three series of copolymers (MMC)	113
Table 4.7 : T_g at the maximum loss modulus for the three series of MMC copolymers	118
Table 4.8 : Characteristic peaks and chemical shifts of ^1H -NMR spectrum of AM2B	126
Table 4.9 : Values of T_g resulting from DSC and molecular weight characteristics of MMBC copolymers.....	127
Table 4.10 : Swelling (%) in crosslinked copolymer of AS1B(10%).....	128
Table 4.11 : Decomposition temperatures and weight loss (%) in the MMBC copolymers	130

Table 4.12 : Some bond dissociation energy	131
Table 4.13 : DMA data for four series of MMBC copolymers using BA	135
Table 5.1 : Solid content of copolymers (MMC) and PMMA for coating application.....	140
Table 5.2 : Classification of adhesion test results	141
Table 5.3 : Set-to-touch, Dry-to-touch and Dry-hard time observed for MMC samples	148
Table 5.4 : Results of adhesion measurement, pencil hardness and water immersion tests on MMC samples.....	149
Table 5.5 : The results of acid, alkali and salt resistance for three series MMC samples ...	153
Table 5.6 : Results of solvent rub tests on MMC samples	154
Table 5.7 : Solid content of the copolymers containing BA, MMBC samples	155
Table 5.8 : Set-to-touch, Dry-to-touch and Dry-hard time observed for MMBC samples..	156
Table 5.9 : Results of adhesion measurement, pencil hardness and water resistance tests for MMBC samples.....	157
Table 5.10 : Acid, alkali and salt resistances for MMBC samples	160
Table 5.11 : Results of solvent resistance test on copolymers coatings (MMBC).....	161

LIST OF SYMBOLS AND ABBREVIATIONS

AIBN	Azobisisobutyronitrile
ASTM	American Society for Testing and Materials
BA	Butyl Acrylate
BPO	Benzoyl peroxide
CDCl ₃	Deuterated chloroform
C _p	Heat capacity at constant pressure
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetry
EA	Ethyl acrylate
E'	Storage modulus
E''	Loss modulus
F _{av}	Average functionality
FTIR	Fourier Transform Infrared analysis
GPC	Gel-Permeation Chromatography
HEA	Hydroxy ethyl acrylate
K	Kelvin
KHP	Potassium hydrogen phthalate
MMA	Methyl methacrylate
M _n	Number average molecular weight
M _w	Weight average molecular weight
MWD	Molecular Weight Distribution

NMR	Nuclear Magnetic Resonance
PA	Phthalic anhydride
PMMA	Poly (methyl methacrylate)
$\tan\delta$	Tangant Delta
T_g	Glass transition
TG	Thermogravimetry
TGA	Thermogravimetry analysis
THF	Tetrahydrofuran

LIST OF APPENDIX

APPENDIX A: $^1\text{H-NMR}$ for macromers and related copolymers (MMC).....	176
APPENDIX B: DSC thermograms for macromers.....	181
APPENDIX C: Overlaid FTIR spectra of macromers, related copolymers (MMC), oleic acid and PMMA.....	183
APPENDIX D: Overlay of GPC chromatograms of AlkOA65, AlkOA28, related copolymers and PMMA.....	184
APPENDIX E: DSC thermograms for copolymers (MMC).....	185
APPENDIX F: TGA thermograms for copolymers (MMC).....	190
APPENDIX G: DMA graphs for copolymers (MMC).....	195
APPENDIX H: FTIR spectra for modified copolymers with BA (MMBC).....	198
APPENDIX I: $^1\text{H-NMR}$ spectra for modified copolymers with BA (MMBC).....	199
APPENDIX J: DSC thermograms for copolymers modified with BA (MMBC).....	203
APPENDIX K: Overlay of GPC chromatograms MMBC samples.....	209
APPENDIX L: TGA thermograms for copolymers modified with BA (MMBC).....	211
APPENDIX M: DMA graphs for copolymers modified with BA (MMBC).....	217
APPENDIX N: Description of Figures 3.12, 3.14, 3.16 and Table 3.20 in Chapter 3.....	221
APPENDIX P: Publications and presentations.....	235