# PREPARATION AND CHARACTERIZATION OF WATERBORNE ACRYLIC LATEX POLYMERS PRESSURE-SENSITIVE ADHESIVES

**by**

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**Thesis submitted in fulfillment of the requirements**
**for the degree**
**of Master of Science**

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## DECLARATION

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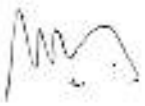

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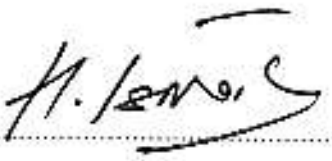

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## TABLE OF CONTENTS


| | | Page |
|---|---|---|
| **ACKNOWLEDGEMENT** | | ii |
| **TABLE OF CONTENTS** | | iii |
| **LIST OF TABLES** | | viii |
| **LIST OF FIGURES** | | ix |
| **LIST OF SYMBOLS** | | xv |
| **LIST OF ABBREVIATIONS** | | xvi |
| **LIST OF PUBLICATIONS** | | xviii |
| **ABSTRAK** | | xix |
| **ABSTRACT** | | xx |
| **CHAPTER ONE – INTRODUCTION** | | |
| 1.1 | Introduction | 1 |
| 1.2 | Problem Statement | 5 |
| 1.3 | Research Objectives | 7 |
| **CHAPTER TWO - LITERATURE REVIEW** | | |
| 2.1 | Pressure-Sensitive Adhesives (PSAs) | 8 |
| | 2.1.1 Solvent-based Adhesives | 11 |
| | 2.1.2 Hot Melt Adhesives | 13 |
| | 2.1.3 Water-based Adhesives | 14 |

2.2 Emulsion Polymerization 16

2.2.1 Definition of Emulsion Polymerization 16

2.2.2 Intervals in Emulsion Polymerization 17

2.2.3 Mechanism of Emulsion Polymerization 20

2.2.4 Semi Batch Emulsion Polymerization 24

2.3 Acrylic Pressure-Sensitive Adhesives 26

2.4 Initiator 27

2.5 Surfactant 28

2.6 Monomer 29

2.6.1 Introduction of Acrylate Monomer 29

2.6.2 Structure and Properties of Acrylate Monomer 30

2.6.2(a) Structure 30

2.6.2(b) Chemical Properties and Characteristic 31

2.7 Factor Affecting Adhesive Properties 34

2.7.1 Monomer Composition 34

2.7.2 Particle Size and Particle Size Distribution 36

2.7.3 Gel Content 38

2.7.4 Glass Transition Temperature 39

**CHAPTER THREE – MATERIALS AND METHODOLOGY**

3.1 Raw Materials 42

3.2 Instruments 43

3.3 Formulation of Emulsion Polymerization 43

3.4 Synthesis of Acrylic PSA 50

3.4.1 Initiator Preparation Step 50

3.4.2 Buffer Solution Preparation Step 51

3.4.3 Monomer Pre-Emulsion Charge 51

3.4.4 Polymerization Procedure 52

3.5 Peel Adhesion of Pressure-Sensitive Tape 54

3.6 Dynamic Shear Test 55

3.7 Loop Tack 56

3.8 Viscosity Test 57

3.9 Total Solid Content 57

3.10 Particle Size Determination 58

3.11 Gel Content Determination 58

3.12 Stereo Zoom Microscope 59

3.13 Glass Transition Temperature 59

3.14 Fourier-Transform Infrared (FTIR) spectroscopy 60

**CHAPTER FOUR - RESULTS AND DISCUSSION**

4.1 Synthesis of Emulsion Polymerization 61

4.2 FTIR Analysis 63

4.3 DSC Analaysis 67

4.4 Effect of Methyl Methacrylate Composition on Adhesive Performance 69

4.4.1 Glass Transition Temperature 70

4.4.2 Peel Strength 71

4.4.3 Dynamic Shear Strength 72

4.4.4 Loop Tack 74

4.4.5 Stereo Zoom Microscope 75

4.4.6 Gel Content 80

4.5 Effect of Acrylic Acid Composition on Adhesive Performance 81

4.5.1 Glass Transition Temperature 82

4.5.2 Peel Strength 83

4.5.3 Dynamic Shear Strength 84

4.5.4 Loop Tack 85

4.5.5 Stereo Zoom Microscope 86

4.5.6 Gel Content 89

4.6 Effect of 2-ethylhexyl Acrylate Composition on Adhesive Performance 90

4.6.1 Glass Transition Temperature 91

4.6.2 Peel Strength 92

4.6.3 Dynamic Shear Strength 93

4.6.4 Loop Tack 94

4.6.5 Stereo Zoom Microscope 95

4.6.6 Gel Content 98

4.7 Effect of Particle Size on Adhesive Performance 99

4.7.1 Glass Transition Temperature 100

4.7.2 Peel Strength 100

4.7.3 Dynamic Shear Strength 101

4.7.4 Loop Tack 102

4.7.5 Stereo Zoom Microscope 103

4.7.6 Gel Content 106

4.8 Comparison between Rosin Ester Dispersion Filled Natural Rubber Latex, Terpene Phenolic Resin Dispersion Filled Natural Rubber Latex and Acrylic PSA Filled Natural Rubber Latex 106

4.8.1 Peel Strength 107

4.8.2 Dynamic Shear Strength 109

4.8.3 Loop Tack 110

**CHAPTER FIVE - CONCLUSIONS AND RECOMMENDATION FOR FUTURE RESEARCH**

5.1 Conclusions 112

5.2 Recommendation for Future Research 114

**REFERENCES** 115

**PUBLICATION** 119

## LIST OF TABLES


| | | Page |
|---|---|---|
| Table 2.1 | Structure of monomers used in polymerization | 31 |
| Table 3.1 | List of raw material used | 42 |
| Table 3.2 | List of instruments and tests/processes involved | 43 |
| Table 3.3 | Formulation of varied MMA composition used for the synthesis of the PSA latexes | 45 |
| Table 3.4 | Formulation of varied AA composition used for the synthesis of the PSA latexes | 46 |
| Table 3.5 | Formulation of varied 2-EHA composition used for the synthesis of the PSA latexes | 47 |
| Table 3.6 | Formulation of different composition of surfactant used for the synthesis of the PSA latexes | 48 |
| Table 3.7 | Formulation of various resin and acrylic PSA loading on Natural Rubber Latex compounds | 49 |
| Table 3.8 | Polymerization procedure for run 1 to run 13 | 53 |
| Table 3.9 | Polymerization procedure for run 14 to run 20 | 53 |
| Table 4.1 | Result of testing of PSAs for run 1 to run 8 | 70 |
| Table 4.2 | Result of testing of PSAs for run 9 to run 13 | 82 |
| Table 4.3 | Result of testing of PSAs for run 14 to run 17 | 91 |
| Table 4.4 | Result of testing of PSAs for run 14, run 18 to run 20 | 99 |

## LIST OF FIGURES


| | | Page |
|---|---|---|
| Figure 2.1 | Typical construction of Pressure-Sensitive Adhesive | 9 |
| Figure 2.2 | A schematic diagram of the micelle nucleation model | 20 |
| Figure 2.3 | A schematic show the mechanism of free radical | 24 |
| Figure 2.4 | Flow chart of a semi batch emulsion polymerization process | 25 |
| Figure 2.5 | Examples of initiator used in emulsion polymerization | 28 |
| Figure 2.6 | Structure of acrylic acid | 30 |
| Figure 2.7 | Structure of 2-ethylhexyl acrylate | 30 |
| Figure 2.8 | Structure of methyl methacrylate | 31 |
| Figure 2.9 | Structure of butyl acrylate | 31 |
| Figure 2.10 | Structure of 2-hydroxyethyl acrylate | 31 |
| Figure 3.1 | Experiment flow chart | 50 |
| Figure 3.2 | Sample specimen for peel adhesion testing | 54 |
| Figure 3.3 | Sample specimen for dynamic shear strength test | 55 |
| Figure 3.4 | The shape and dimensions of loop tack specimen | 56 |
| Figure 4.1 | Initiation stage | 62 |
| Figure 4.2 | Propagation and backbiting stage | 62 |
| Figure 4.3 | Intermolecular chain transfer to polymer | 63 |
| Figure 4.4 | Termination step by combination and disproportionation | 63 |
| Figure 4.5 | Polymer chain of acrylic PSA for run 1 to 8 | 64 |
| Figure 4.6 | Polymer chain of acrylic PSA for run 9 to 13 | 64 |

| | | |
|---|---|---|
| Figure 4.7 | Polymer chain of acrylic PSA for run 14 to 20 | 64 |
| Figure 4.8 | The FTIR spectra of (2-EHA/AA/MMA) for Run 3 | 65 |
| Figure 4.9 | The FTIR spectra of (2-EHA/AA) for Run 9 | 66 |
| Figure 4.10 | The FTIR spectra of (BA/AA/2-EHA/2-HEA) for Run 17 | 66 |
| Figure 4.11 | (a) The heating cycle for run 4 (b) The cooling cycle for run 4 | 68 |
| Figure 4.12 | The effect of MMA/2-EHA monomer ratio on Tg of PSA (AA was fixed at 12.5% BOTM) | 71 |
| Figure 4.13 | The effect of MMA/2-EHA monomer ratio on peel strength of PSA (AA was fixed at 12.5% BOTM) | 72 |
| Figure 4.14 | The effect of MMA/2-EHA monomer ratio on dynamic shear strength of PSA (AA was fixed at 12.5% BOTM)) | 73 |
| Figure 4.15 | The effect of MMA/2-EHA monomer ratio on loop tack of PSA (AA was fixed at 12.5% BOTM)) | 75 |
| Figure 4.16 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 0/87.5% MMA/2-EHA content (AA was fixed at 12.5% BOTM) at magnification 45X | 76 |
| Figure 4.17 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 1/86.5% MMA/2-EHA content (AA was fixed at 12.5% BOTM) at magnification 45X | 76 |
| Figure 4.18 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 3/84.5% MMA/2-EHA content (AA was fixed at 12.5% BOTM) at magnification 45X | 77 |
| Figure 4.19 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 5/82.5% MMA/2-EHA content (AA was fixed at 12.5% BOTM) at magnification 45X | 77 |

| | | |
|---|---|---|
| Figure 4.20 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 7/80.5% MMA/2-EHA content (AA was fixed at 12.5% BOTM) at magnification 45X | 78 |
| Figure 4.21 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 9/78.5% MMA/2-EHA content (AA was fixed at 12.5% BOTM) at magnification 45X | 78 |
| Figure 4.22 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 11/76.5% MMA/2-EHA content (AA was fixed at 12.5% BOTM) at magnification 45X | 79 |
| Figure 4.23 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 13/74.5% MMA/2-EHA content (AA was fixed at 12.5% BOTM) at magnification 45X | 79 |
| Figure 4.24 | The effect of MMA/2-EHA monomer ratio on gel content of PSA (AA was fixed at 12.5% BOTM) | 81 |
| Figure 4.25 | The effect of AA/2-EHA monomer ratio on Tg of PSA | 83 |
| Figure 4.26 | The effect of AA/2-EHA monomer ratio on peel strength of PSA | 84 |
| Figure 4.27 | The effect of AA/2-EHA monomer ratio on dynamic shear strength of PSA | 85 |
| Figure 4.28 | The effect of AA/2-EHA monomer ratio on loop tack of PSA | 86 |
| Figure 4.29 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 5/95% AA/2-EHA content at magnification 45X | 87 |

| | | |
|---|---|---|
| Figure 4.30 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 7.5/92.5% AA/2-EHA content at magnification 45X | 87 |
| Figure 4.31 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 10/90% AA/2-EHA content at magnification 45X | 88 |
| Figure 4.32 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 12.5/87.5% AA/2-EHA content at magnification 45X | 88 |
| Figure 4.33 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after dynamic shear strength testing and (b) Kraft paper at 15/85% AA/2-EHA content at magnification 45X | 89 |
| Figure 4.34 | The effect of AA/2-EHA monomer ratio on gel content of PSA | 90 |
| Figure 4.35 | The effect of 2-EHA/BA monomer ratio on Tg of PSA (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) | 92 |
| Figure 4.36 | The effect of 2-EHA/BA monomer ratio on peel strength of PSA (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) | 93 |
| Figure 4.37 | The effect of 2-EHA/BA monomer ratio on dynamic shear strength of PSA (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) | 94 |
| Figure 4.38 | The effect of 2-EHA/BA monomer ratio on loop tack of PSA (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) | 95 |

| | | |
|---|---|---|
| Figure 4.39 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after shear strength testing and (b) Kraft paper at 0/97% 2-EHA/BA content (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) at magnification 45X | 96 |
| Figure 4.40 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after shear strength testing and (b) Kraft paper at 4/93% 2-EHA/BA content (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) at magnification 45X | 96 |
| Figure 4.41 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after shear strength testing and (b) Kraft paper at 8/89% 2-EHA/BA content (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) at magnification 45X | 97 |
| Figure 4.42 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after shear strength testing and (b) Kraft paper at 12/85% 2-EHA/BA content (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) at magnification 45X | 97 |
| Figure 4.43 | The effect of 2-EHA/BA monomer ratio on gel content of PSA (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) | 98 |
| Figure 4.44 | The effect of latexes particle size on glass transition temperature of PSA | 100 |
| Figure 4.45 | The effect of latexes particle size on peel strength of PSA | 101 |
| Figure 4.46 | The effect of latexes particle size on dynamic shear strength of PSA | 102 |
| Figure 4.47 | The effect of latexes particle size on loop tack of PSA | 103 |
| Figure 4.48 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after shear strength testing and (b) Kraft paper at 1.67% ABEX 8018 content BOTM (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) at magnification 45X | 104 |

| | | |
|---|---|---|
| Figure 4.49 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after shear strength testing and (b) Kraft paper at 2% ABEX 8018 content BOTM (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) at magnification 45X | 104 |
| Figure 4.50 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after shear strength testing and (b) Kraft paper at 2.5% ABEX 8018 content BOTM (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) at magnification 45X | 105 |
| Figure 4.51 | Stereo zoom microscope photos of the adhesive residue on (a) testing sheets after shear strength testing and (b) Kraft paper at 3% ABEX 8018 content BOTM (2-HEA was fixed at 2% BOTM and AA was fixed at 1% BOTM) at magnification 45X | 105 |
| Figure 4.52 | The effect of latexes particle size on gel content of PSA | 106 |
| Figure 4.53 | Variation in peel strength with various resin and acrylic PSA loading | 108 |
| Figure 4.54 | Variation in dynamic shear strength with various resin and acrylic PSA loading | 110 |
| Figure 4.55 | Variation in loop tack with various resin and acrylic PSA loading | 111 |

## LIST OF SYMBOLS

| | |
|---|---|
| Tg | Glass Transition Temperature |
| % | Percentage |
| dp | Number Average Particle size |
| wt% | Percentage in weight |
| $^{O}C$ | Degree Celcius |
| nm | Nanometer ($10^{-9}$ metre) |
| mm | Milimeter ($10^{-3}$ metre) |
| N | Newton |
| $cm^2$ | Centimeter square |
| g | Gram |
| min | Minute |
| cps | Centipose |
| wt | Weight |

## LIST OF ABBREVIATIONS

| | |
|---|---|
| AA | Acrylic acid |
| ASTM | American Society for Testing and Materials |
| ATR | Attenuated Total Reflectance |
| BA | Butyl acrylate |
| BOTM | Based on total monomer |
| C | Carbon |
| CMC | Critical micelle concentration |
| EVA | Ethylene-vinyl acetate |
| DI | Deionized water |
| DSC | Differential Scanning Calorimetry |
| FTIR | Fourier-Transform Infrared Spectroscopy |
| H | Hydrogen |
| M | Monomer |
| MMA | Methyl methacrylate |
| NR | Natural Rubber |
| PSTC | Pressure-sensitive Tape Council |
| PSA | Pressure-sensitive adhesive |
| PSAs | Pressure-sensitive adhesives |
| R | Radical |
| phr | Part per hundred resin |
| THF | tetrahydrohuran |

| | |
|---|---|
| VOC | Volatile organic compound |
| 2-EHA | 2-ethylhexyl acrylate |
| 2-HEA | 2-hydroxylethyl acrylate |

## LIST OF PUBLICATIONS


| | | Page |
|---|---|---|
| Appendix A | Yew, F.W., Ismail, H., Ahmad, Z. Effect of Monomer Composition on Adhesive Performance for Waterborne Acrylic Pressure-sensitive Adhesives, *Journal of Physical Science*, Vol. 22(2), 51–63, 2011. | 119 |
| Appendix B | Yew, F.W., Ismail, H., Ahmad, Z. Effect of 2-ethylhexyl acrylate Composition on Adhesive Performance for Waterborne Acrylic Pressure-sensitive Adhesives. 4th Colloquium on Postgraduate Research, Postgraduate Colloquium on Materials, Mineral, and Polymers 2009 (MAMIP 2009). Vistana Hotel, Penang. (Oral Presenter) | 120 |
| Appendix C | Yew, F.W., Ismail, H., Ahmad, Z. Adhesive Performance of Acrylic Pressure-Senstive Adhesives Prepared by Emulsion Polymerization of 2-ethylhexyl acrylate/Methylmethacrylate/Acrylic Acid. National Symposium on Polymeric Materials 2010, Awana Porto Malai Resort, Langkawi. (Oral Presenter) | 121 |

**PENYEDIAAN DAN PENCIRIAN PEREKAT SENSITIF TEKANAN POLIMER LATEKS AKRILIK KANDUNG AIR**

## ABSTRAK

Perekat sensitif tekanan akrilik yang disediakan dengan kaedah pempolimeran emulsi merupakan perekat mesra alam. Monomer yang digunakan dalam sintesis ini terdiri daripada butil akrilat (BA), asid akrilik (AA), 2-etilheksil akrilat (2-EHA), metil metakrilat (MMA) dan 2-hidroksiletil akrilat (2-HEA). Sifat-sifat perekat dikaji dengan mengubah nisbah monomer yang berlainan. Saiz partikel diukur dengan menggunakan penghurai laser saiz partikel CILAS 1180. Spektroskopi ATR-FTIR digunakan untuk menentukan nombor gelombang emulsi akrilik yang diperoleh. Emulsi akrilik seterusnya disalut dengan ketebalan perekat yang sama pada kertas Kraft untuk menyediakan spesimen untuk mengkaji sifat-sifat perekat termasuk jelujur gelung, kekuatan pengupasan, dan kekuatan ricih dinamik. Kekuatan pengupasan bertambah dan jelujur gelung berkurang apabila komposisi MMA dan AA bertambah. Ikatan hidrogen yang terbentuk daripada kumpulan berfungsi asid karboksilik menyebabkan kekuatan pengupasan bertambah. Kandungan gel berkurang apabila komposisi MMA bertambah. Kekuatan ricih dinamik didapati berkurang apabila kandugan gel berkurang. Kekuatan ricih dinamik dan kekuatan pengupasan bertanbah apabila komposisi 2-EHA meningkat. Kekuatan pengupasan dan kekuatan ricih dinamik bertambah apabila saiz partikel emulsi akrilik berkurang.

**PREPARATION AND CHARACTERIZATION OF WATERBORNE ACRYLIC LATEX POLYMERS PRESSURE-SENSITIVE ADHESIVES**

## ABSTRACT

Acrylic pressure-sensitive adhesives obtained by emulsion polymerization are environmental friendly adhesives. The monomers chosen were butyl-acrylate, acrylic acid, 2-ethylhexyl acrylate, methyl methacrylate, and 2-hydroxyethyl acrylate. The effect of varied monomer composition on adhesive performance is studied. The particle sizes of adhesives were measured by using CILAS 1180 Laser Particle Size Analyzer. ATR-FTIR spectroscopy was used to determine the wave number of acrylate emulsions obtained. The adhesives obtained with constant thickness were coated onto a Kraft paper and evaluated for adhesive performance by measuring their loop tack, peel strength and dynamic shear strength. With increasing of MMA and AA content, peel strength was found to increase and loop tack decreased. Hydrogen bond formed through the carboxylic acid functional group increased the peel strength. As the MMA content increased, the latex gel fractions were found to decrease. With decreasing of gel fraction, dynamic shear strength was found to decrease. As the 2-EHA content increased, dynamic shear strength and peel strength were found to increase. Peel strength and dynamic shear strength showed an increase with decreasing of particle size.

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

Adhesives are defined as substances capable of holding at least two surfaces together. A class of adhesives called pressure-sensitive adhesive (PSA) is characterized by instantaneous adhesion upon application of light pressure (Benedek and Feldstein, 2009). No solvent, water or heat is needed to activate the adhesive. It is used in pressure-sensitive tapes, labels, note pads, automobile trim and a wide variety of other product (Satas, 1989). The degree of bonding is influenced by the amount of pressure applied. PSAs typically designed to form a bond and hold properly at room temperature. PSAs can be classified according to their adhesive and their use. Classifications of PSAs differ according to their physical status, their bond character, and their environmental resistance. There are three different types of PSAs according to adhesive physical status which used commercially today. They can be divided into solvent-based, water-based, and hot melt adhesives (Benedek and Feldstein, 2009).

Originally PSA products were manufactured by drying a solution of the adhesive on the suitable backing. An important consideration in solvent selection is air pollution requirement. In recent years, increasing social and political awareness, coupled with the tightening of worldwide environmental legislation such as strict volatile organic compound (VOC) level reduction as required by the EPA Clean Air Act Title 5 (United States Environmental Protection Agency, 1990), has forced coating industries to decrease levels of pollutant substances released to the

atmosphere. Solvents from the coating industry are considered to be volatile organic substances. For this reason there is an increasing tendency to move away from conventional solvent-borne coating to those that use water as fluid vehicle (Tigh and Evren, 2005).

Acrylic polymers are widely used as pressure-sensitive adhesives (PSAs). The first use of acrylic acid esters as pressure-sensitive adhesives is generally attributed to Walter Bauer working at the Rohm and Hass Company in 1928. Acrylic polymers are available as solvent-based, water-based, and 100% solid. Acrylic PSAs obtained by emulsion polymerization currently hold the biggest share of the PSA market. Emulsion polymerization is a unique process widely used to produce waterborne resins with various colloidal and physicochemical properties. It involves the propagation reaction of free radical with monomer molecules in a very large number of polymer particles dispersed in continuous aqueous phase. Acrylic PSAs used extensively in end-use markets that demand excellent color and clarity, weatherability, durability, and plasticizer migration resistance. The advantages of acrylic PSAs include chemical and water resistance, UV and oxidative stability, heat resistance, tack at varying temperatures, and the balance of adhesive and cohesive properties (Benedek and Feldstein, 2009). Their success is attributable, in part, to the replacement of flammable and environmentally unfriendly solvents with water. Other advantages of acrylic PSAs are their high solid content, their ease of application, and the fact that they may be formulated, in many instances, without the need for addition of tackifiers (Gower and Shanks, 2004).

Focusing on water-based acrylic PSAs, there are numbers of studies relating the effects of monomer composition to the adhesive performance of the PSAs (Gower and Shanks, 2004, Jovanovic *et al.*, 2004, Tobing and Klein, 2001). They found that acrylic PSAs can be tailored to control the polymer glass transition temperature (Tg), the gel content, and the molecular characteristics. Polymer of acrylic and methacrylic esters that yield low Tg and high molecular weights are the basis of acrylic PSAs. Commercially, the main monomers used for their preparation are butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA). However to increase the room temperature performance of these soft acrylic homopolymers, it is necessary to increase their Tg. Increasing the polymer Tg can be accomplished by copolymerizing with one or more high Tg monomers such as methyl methacrylate (MMA; Tg = 105$^{o}$C), acrylic acid (AA; Tg = 106$^{o}$C), or any of a number of hardening monomers.

In early studies, Mao and Reegen (1962) noted that for acrylic monomers copolymerized with MMA, the peel strength increased as the number of carbon atoms in the side chain of the co monomers increased. Work by Britton *et al*. (2001) showed that the introduction of MMA into acrylate copolymerization reduces the levels of branching and measurement of gel contents of emulsion polymers. Araujo *et al*. (2001) revealed that copolymerized MMA serves to lower gel contents. Increasing amount of carboxylic acid react in increase in gel content and decrease in loop tack. Effect of carboxylic acid was studied by comparing the peel master-curves which peel adhesion increased when carboxylic incorporated in the adhesive formulation (Aubrey and Ginosatis, 1980). In addition, monomers with functional groups such as acrylic acid (AA) and methacrylic acid (MAA) could be added to improve peel and shear strength although their additions often reduce tack

(Jovanovic *et al.*, 2004). As 2-ethylhexyl acrylate content increased, latex gel fraction was found to increase through higher levels of intermolecular chain transfer to polymer as a result of an overall increase in the tendency for chain transfer, and peel strength also increase. A work was performed on the effect of incorporating 2-ethylhexyl acrylate in PSAs (Gower and Shanks, 2004). The results showed an increased in gel content as the polymer weight fraction of EHA increases.

Loop tack is an adhesive performance indicator often used within industry to gain a measure of the capability of a PSA to adhere immediately to a substrate under light pressure. Tackiness should increase when the Tg of the copolymer decreases and Tg should in turn decrease when the copolymer composition is enriched with a soft polymer like poly(BA) and poly (2-EHA). At low Tg of waterborne acrylic latexes, polymers are flowable and interactions between adhesive and surface are more intensive. Druschke (1989) reported that tack increased for acrylic homopolymers as Tg decreased; this is consistent with the work of Aubrey and Ginosatis (1980). They found that incorporation of low Tg monomer such as BA and 2-EHA can increase the loop tack.

Dynamic shear strength is the resistance of an adhesive coated label stock on a standardized surface, to shear at a constant rate (Benedek and Heymans, 1997). Dynamic shear strength increases as the concentration of 2-EHA increases. The higher dynamic shear strength with increasing of 2-EHA content was due to entanglements of the ethylhexyl side groups (Gower and Shanks, 2004). Polymer containing AA will be expected to form networks through secondary valence forces resulting from hydrogen bonding, thus increasing dynamic shear strength.

Peel adhesion is defined as the force required in removing pressure-sensitive coated material, which has been applied to a standard test plate. According to ASTM D330, Test Method A was chosen which gives a measure of the adherence when peeled at $180^{o}$ angle, to a standard test panel for a single coated tape. For acrylic monomers copolymerized with MMA, the peel strength increased as the number of carbon atoms in the side chain of the co monomers increased (Mao and Reegen, 1962). The presence of MMA increases the hardness of copolymer thus increasing the adhesive strength.

Despite the common knowledge that the particle size of polymer latexes can influence the final properties, therefore little work has been dedicated to study the influence of particle size in adhesive properties. A work was performed to study the effect of particle size and composition on the performance of poly(styrene-co-butyl acrylate) adhesives. The positive effect of smaller particles on shear strength relates to the smaller particles could pack more tightly together during the drying process, thus increasing the area of contact between the adhesive and the substrate (Dube and Stephane, 2006).

## 1.2 Problem Statement

In solvent-based PSAS, the increasing cost of solvent and regulatory restriction regarding emission will restrict their application as PSAs. In recent years, industries turned to water-based and hot melt adhesive and great effort has been dedicated to further understand the adhesive performance of acrylic PSAs prepared

from emulsion polymerization as hot melt adhesive need higher technology and set up cost and is most suitable for large scale production of the same basic product.

Despite the aggressive efforts to substitute solvent-based PSAs, there are still high performances applications that can only met by solvent-based PSAs. The majority of these applications require high cohesive strength and good tack. This is due to the continuous networks in the film by post curing technique. Waterborne acrylic latex characterized by well-balanced composition of copolymer is not commercially available in the market. Their composition, synthesis method and technical details are hidden from producers. This research was focused on the relationship between the effects of monomer composition on adhesive performance of the PSA. For the sake of well film formation performance, the emulsion adhesives are very soft, weak, and tack polymers (Lei *et al.*, 2010). The selection of suitable acrylic monomers for the adhesives is dedicated by the intended application of the PSA and the desired end-product properties (Jovanovic *et al.*, 2004). Other advantages of acrylic PSAs are their high solids, their ease of application, and the fact that they may be formulated, in many instances, without the need for addition of tackifiers (Gower and Shanks, 2004). Despite these issues, it is envisaged that with further improvement and understanding of adhesive performance of acrylic PSAs will find their areas of applications in the coating industry.

## 1.3 Research Objectives

The aim of this research was to obtain a waterborne acrylic PSAs with well-balanced copolymer composition using emulsion polymerization. The adhesive performance of waterborne acrylic PSAs need to be studied in order to substitute solvent-based systems by water-borne products. Hence, the research was divided in 3 phases:

1. The effect of methyl methacrylate, acrylic acid and 2-ethylhexyl acrylate composition on adhesive performance.
2. The effect of particle size of acrylic latex on adhesive performance
3. The comparison between rosin ester dispersion filled natural rubber latex, terpene phenolic resin dispersion filled natural rubber latex and acrylic PSA filled natural rubber latex

For part 1 and part 2, the testing were loop tack, peel strength, dynamic shear strength, FTIR, DSC and stereo zoom microscope. Loop tack, peel strength, dynamic shear strength are important adhesive properties that determine PSA performance. The FTIR was conducted to measure the functional group after emulsion polymerization Thermal test was focused on differential scanning calorimetry (DSC) to determine the Tg of latexes obtained. The stereo zoom microscope photos was carried out to observe the adhesive residue on Kraft paper and testing sheets after dynamic shear strength testing. Meanwhile, adhesive performance test only been conducted for part 3 to compare the effect of loading of resin and acrylic PSAs obtained in natural rubber latex.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Pressure-Sensitive Adhesives (PSAs)

Pressure-sensitive adhesive (PSA) is adhesive which forms a bond when pressure is applied to join the adhesive with the adherend. No solvent, water or heat is needed to activate the adhesive. It is used in pressure-sensitive tapes, labels, note pads, automobile trim and a wide variety of other product (Satas, 1989). The degree of bond is influenced by the amount of pressure apply. PSA typically designed to form a bond and hold properly at room temperature. It reduces and loses their tack at cold temperature and reduces their shear holding ability at high temperature. It is important to choose an adhesive formulation which is designed for its intended use condition.

PSAs can be classified according to their adhesive and their use. Classifications of PSAs differ according to their physical status, their bond character, and their environmental resistance (Benedek and Feldstein, 2009). There are three different types of PSAs according to adhesive physical status which used commercially today. They can be divided into solvent-based, water-based, and hot melt adhesives. In some application domains a permanent adhesive joint is needed; in other end-use domains removable adhesive is required. To form a permanent bond, structural adhesives harden via processes such as evaporation of solvent or water, reaction with UV radiation or cooling which applied in hot melt adhesives. In contrast, removable PSAs can be peeled off easily. Peel resistance and removability can be controlled by regulating the ratio between the adhesion surface and the

application surface. The environmental resistance of PSAs includes their chemical, temperature and aging resistance (Benedek and Feldstein, 2009). PSA are designed with a balance between flow and resistance to flow. The bond has strength because the adhesive is hard enough to resist flow when stress is applied. PSA products basically consist of an adhesive coated on a backing or carrier. The backing is flexible film, foil, fabric. A typical construction is shown in below

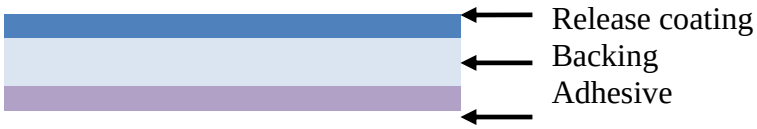



Figure 2.1: Typical construction of Pressure-Sensitive Adhesive

Originally PSA products were manufactured by drying a solution of the adhesive on the suitable backing. An important consideration in solvent selection is air pollution requirement. Solvents from the coating industry are considered to be volatile organic substances. For this reason there is an increasing tendency to move away from conventional solvent-borne coating to those that use water as fluid vehicle (Tigh and Evren, 2005). At the December 2009, United Nations Climate Change Conference in Copenhagen, the nations have agreed to adopt national policies and take corresponding measures towards climate change mitigation by limiting VOC emission. Due to increasing cost of solvent and regulatory restriction regarding emission, industry find an alternative way to produce water-based and hot melt adhesive.

Pressure-sensitive adhesives are unusual materials in the sense which somewhere in between the viscous and rubber states at room temperature, that is, their response to deformation is viscoelastic. They show sufficient liquid-like

behavior to deform of flow into contact with a smooth surface under light contact with appreciable resistance to flow during a separation or "debonding" process. The special feature of pressure-sensitive adhesives is that they do not solidify to form a solid material, but remain viscous. As a result, they remain permanently tacky and have the ability to wet surfaces on contact. Bonds are made by bringing the adhesive film in contact with the substrate and applying pressure. If inadequate pressure is applied or the processing temperature is too low, bonding faults such as bubbles or detachment can occur.

The advantages of pressure-sensitive adhesives compared with other types of adhesives are those of convenience to use. There is no storage problem, there is no mixing or activation necessary and no waiting is involved. Often the bond is readily reversible. However, the disadvantages are that their adhesive strength, both peeling and shearing strengths are low, unsuitable for rough surfaces and they are expensive in terms of cost per unit bond area.

As discussed earlier, pressure-sensitive adhesives are available as solvent-based, water-based and hot melt adhesives, which lead to different performance characteristic. Generally, each adhesive type can be used for the whole range of pressure-sensitive products. The selection of material to be used as a based not only on the final adhesion properties required but also on considerations the cost of the manufacturing process for the particular pressure-sensitive product. The interest in the emulsion polymers is increasing due to the need to solve the solvent emission problems and produce more environmentally friendly products. Hence the solution polymerization was replaced with emulsion polymerization processes which are

relatively simple methods for production of PSAs. They do not require high temperature and pressure.

### 2.1.1 Solvent-based Adhesives

Solvent-based adhesives are a mixture of ingredients typically polymers such as natural rubber (NR), butyl rubber, and polyacrylate copolymer dissolved in a solvent. The performance of solvent-based adhesives is largely determined by the polymer system in the formulation. Most solvent-based adhesives contain flammable solvents which require proper precautions for safe handling. In addition, many organic solvents are regulated due to environmental concerns with emissions. Once the adhesive is applied, solvent evaporates relatively quickly causing an increase in viscosity of the adhesive film. Bonds can be formed immediately after adhesive application or after some solvent has evaporated but before the adhesive has dried to the point where it will no longer exist. Their advantage lies in the rapid initial bond strength between the bonded parts and their suitability for outdoor applications.

The most well-known type of adhesive consists of natural rubber blended with an approximately equal amount of a tackifier resin, and a small amount of antioxidant. It is applied to a suitably supporting member or backing, such as regenerated cellulose film. A release agent on the reverse side of the backing is commonly applied to facilitate unwinding. Early rosin tackifier resins were later replace by better aging terpene resins, which in turn have now been largely replace for economic reasons by cheaper resins obtained by the cationic polymerization of

petroleum factions, C4, C5, C6, although the terpene resins are still regarded as being technically excellent. The viscosity and shear strength of pressure-sensitive adhesives based on natural rubber were studied with gum rosin and petroresin as the tackifying resins (Poh *et al*, 2008 A). The shear strength decreased gradually with increasing resin content for both tackifying resins due to the dilution effect of the resins. The pressure-sensitive adhesives prepared from natural rubber / epoxidized natural rubber blends were investigated using coumarene-indene resin as the tackifier to study the adhesion properties (Poh and Lim, 2008 B). Increasing wettability of adhesive and compatibility between rubbers with blend ratio enhances the peel strength of the adhesive up to a certain level.

Usage of solvent in solvent-based adhesives may be achieved by the higher solution concentrations possible from the use of the newer thermoplastic rubbers, especially styrene-isoprene-styrene, in place of some or all of the natural rubber, and this is quite commonly practiced in current solution coatings. Rigid PVC and polypropylene are now also extensively used as backing materials for general purpose pressure-sensitive adhesives tapes, and many other plastic films and paper used in specialized products including tapes, labels and decals.

Another type of solution coating extensively used is that based on polyacrylate or an acrylate-vinyl acetate copolymer. These are generally used in high quality tapes for their better technical properties; they are paler in colour, much better aging, and if cross-linked after coating can give very good shear strength. Other adhesives polymers used to a lesser extent in solution coating are polyvinyl alkyl ethers, polyisobutylenes, and silicones.

Butyl rubber and polyisobutylene are soluble in hydrocarbon and chlorinated solvent. Volatile paraffinic solvents such as hexane are used. The present of minor amounts of stabilizer and metal stearate in butyl rubber and PIB may cause pure gum to be slightly cloudy. These materials will slowly settle out of low viscosity solution of the polymer. The settling can be avoided by working with higher viscosity solution.

### 2.1.2 Hot Melt Adhesives

Hot melt adhesives are applied in molten forms which solidify on cooling to form strong bonds between a wide range of materials. Early hot melt adhesives were based on ethyl cellulose and animal glues made by rendering animal product and casein. These were later replaced with synthetic resins such as polyamide. The most recent development in pressure-sensitive tape manufacture is the development of the hot-melt coating process. Almost all of the current hot-melt applied adhesives are based on styrene-isoprene-styrene thermoplastic rubber, mixed with hydrocarbon tackifier resins and oils in substantial amounts, and an antioxidant in minor amounts. Adhesive performance of hot melt PSAs based on styrenic block polymers were discussed. The adhesive performance of styrenic block copolymer hot melt PSA can be improved by incorporating rosin resin, terpene resin or hydrocarbon resin (Park and Kim, 2006). Usually, the materials are mixed in an extruder and fed via a holding tank direct to the coating head. It is therefore a very fast and economical process but is not very versatile and is expensive to set up the production line. The polymer forms the backbone of the adhesive, providing strength and toughness. The tackfying resin contributes surface wetting and tack, while petroleum wax is used to

lower melt viscosity, reduce cost, and control setting speed. Antioxidant, fillers, blowing agent can used to enhance certain properties.

Most recently a new class of compounds referred to block copolymers of styrene and butadiene which tend to widen the flexibility property range of hot melt adhesive. Their primary application is in hot melt PSA. The advantages of hot melt are rapid set time produces an increase in production rate, hot melt dispensing is easy to automate, the elimination of solvent recovery or disposal cost, elimination of hazardous chemical, smaller space requirement for both storage and use, reduced maintenance and cleanup cost and wide formulating latitude to meet cost and performance of end uses.

### 2.1.3 Water-Based Adhesives

Under the volatile organic compounds (VOC) regulations strengthened from the viewpoint of environmental protection, waterborne surface coating resin has been an important research topic all over the world. In Europe, the issue has been addressed via the European Directive 1999/13/EC on the limitation of emissions of VOCs due to the use of organic solvents in certain activities and installations. Industrial sectors covered by the Directive include surface cleaning, coating and adhesive. Most of the signatory countries of Organization for Economic Cooperation and Development agreed to a 30% reduction in emissions of VOCs by 1999 using a year between 1984 and 1990 as a basis (Tigh and Evren, 2005).

The use of organic solvents for coating is becoming increasingly unpopular and various means have been sought to eliminate the solvent. Latex is any emulsion

in water of finely divided particle of synthetic rubber or plastic used in paints, adhesives. Latexes may be natural or synthetic. Natural latex refers to material obtained primarily from the rubber tree. Synthetic latexes are aqueous dispersion of polymers obtained by the process of emulsion polymerization. These include polymers of chloroprene, butadiene-styrene, vinyl-acetate, acrylate, and vinyl-chloride. The use of latex rather than solvent-based system for rubber or resin adhesives has not resulted in commercial success due to dispersion, mechanical stability, film homogeneity and cost of drying problem. However, emulsion systems based on polyacrylate emulsions have been developed successfully as pressure-sensitive adhesives and are widely used in sheet materials and labels. These materials do not need added tackifier resins and are very stable mechanically, so the above problems are largely eliminated.

Water-based adhesives use water as the carrier fluid, with the adhesive particles suspended in water, reducing the adhesive's viscosity so that it can be applied to various substrates at varying thicknesses. Some uses of water-based adhesive are labels, packaging, wood bonding, fabric bonding, panel lamination, high pressure laminate bonding, construction, bonding of floor and wall tiles and tapes. Generally water-based acrylic PSAs posses a higher solid content than common ethylene-vinyl acetate (EVA) emulsion. Water-based acrylic PSAs demonstrate better wet-out properties than other emulsion and can be converted at higher speeds.

## 2.2 Emulsion Polymerization

### 2.2.1 Definition of Emulsion Polymerization

Emulsion polymerization is a type of radical polymerization that widely used to produce waterborne latexes polymers with various colloidal and physicochemical properties. The process involves emulsification of the relatively hydrophobic monomer in water by oil-in-water emulsifier, followed by initiation reaction with water soluble initiator eg: potasium persulfate, tert-butyl hydroperoxide (TBHP) or oil soluble initiator. An emulsifier is a substance that stabilizes an emulsion by increasing its kinetic stability. One class of emulsifiers is known as surface active substances, or surfactants. An effective surfactant such as ionic or non-ionic surfactants and protective colloid such as polyvinyl alcohol which can be adsorbed onto the particle surface is required to prevent the interactive latex from coagulation. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer are emulsified with surfactants in a continuous phase of water. Emulsions are part of a more general class of two-phase systems of matter called colloids, which refers to a dispersion of particles or droplets through a liquid. Although the terms colloid and emulsion are sometimes used interchangeably, emulsion tends to imply that both the dispersed and the continuous phase are liquid.

This emulsion polymerization finds a wide range of application such as synthetic rubber, thermoplastic, coating, adhesives, rheological modifier, plastic pigment. To gain a fundamental understanding of polymerization mechanisms and kinetics is a must in designing quality products that fulfill customers' requirements.

### 2.2.2 Intervals in Emulsion Polymerization

Emulsion polymerization formulation comprises monomer, water, surfactant and water soluble initiator. Surfactant acts as emulsifier to establish particle nucleation and to stabilize the particles against flocculation. The reaction is characterized by emulsified monomer droplet dispersed in the continuous aqueous phase with the aid of surfactant at the beginning of polymerization. Only a small fraction of relatively hydrophobic monomer is present in the micelles or dissolved in the aqueous phase. Most of the monomer molecules dwell in the monomer droplets. Micelles are an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic head regions in contact with surrounding solvent, sequestering the hydrophobic single tail regions in the micelle centre.

Initially the polymerization begins with the present of initiator. In the micelle nucleation model that studied by Harkins (1946 and 1947) and Smith and Ewart (1948) and modified by Gordon (1968), suggested that submicron latex particles (ca. 0.005-1 μm in diameter, $10^{16}$-$10^{18}$ $dm^{-3}$ in numbers) are generated through the capture of free radicals by micelles which exhibit an extremely largely oil-water interfacial area. Radicals are formed and these radicals are too hydrophilic to enter the organic phase of the system, they react with the monomer in aqueous phase, forming oligoradicals. After adding some monomer units, the oligoradicals become hydrophobic enough to be able to enter the micelles. Entry of radical into monomer droplets is not likely as their surface area is much lower than micelles. Due to high concentration of monomer in the micelles, oligoradicals that has entered micelles grows fast, forming polymer chain. The new species formed upon entry of radical

into micelles is considered to be polymer particle. The process of formation of polymer particles by entry of radicals into the micelles is called heterogeneous nucleation. The oligoradicals that do not enter micelles will continue to grow and upon reaching some critical length, they become too hydrophobic and precipitate. This emulsifier present in the system will adsorb onto the newly formed interface, thus stabilizing the polymer. Then, monomer will diffuse into the new polymer particle. This process is called homogenous nucleation (Gordon, 1968 A).

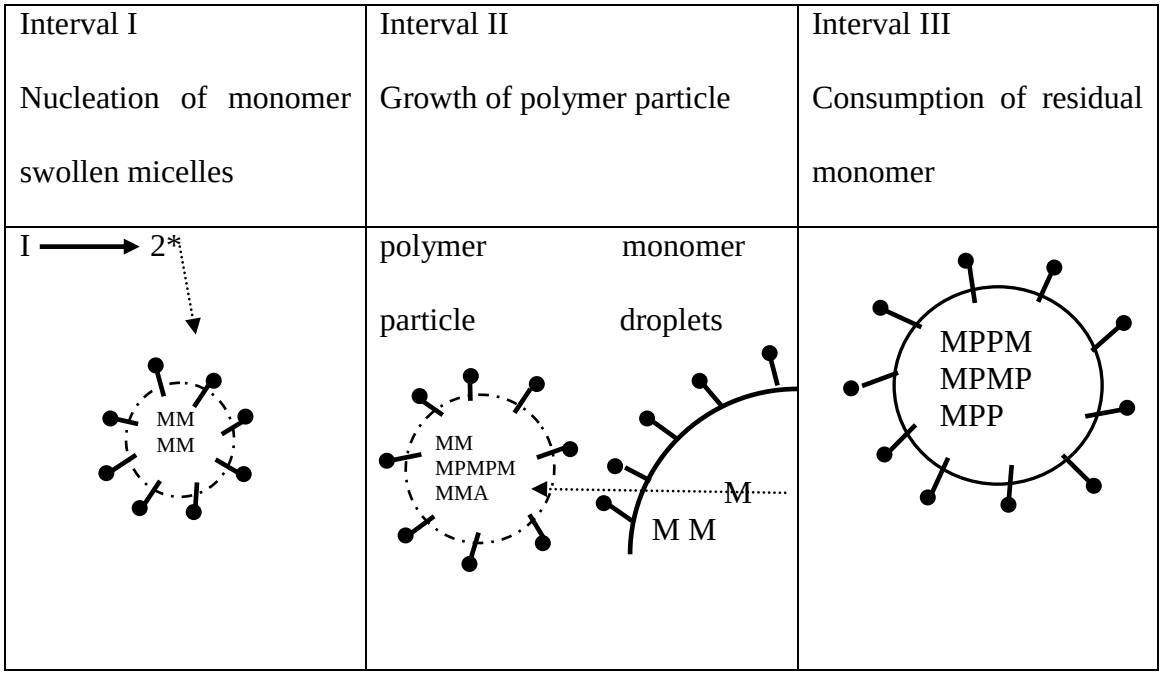
During nucleation, monomer droplets, monomer swollen micelles, monomer swollen polymer particles coexist. Polymer particles compete for radicals, hence monomer is consumed by polymerization inside the polymer particles. The monomer that is consumed replace by monomer that diffused from monomer droplets. Therefore, size of particle increase and that monomer droplets decrease. The numbers of micelles decrease because the entering monomers become polymer upon entry of radical. The surfactant molecules in the micelles become absorb homogenously into the growing particles hence stabilizing the system. The particles are assumed to grow until another free radicals enters to terminate the reaction. Growth resumes when a new free radical enters the particle.

Particle nucleation controls the particle size and particle size distribution of latex products. It is the transport of the free radicals between the continuous aqueous phase and particles that determines the average number of free radical per particle during polymerization. Free radicals generated in the aqueous can be absorbed by the particles during interval II. For example, an idle particle becomes active in the propagation reaction immediately after the capture of 1 free radical. In addition to the

major propagation reaction, 1 free radical may undergo the bimolecular termination reaction with another free radical. Desorption of the free radical out of the particles may also take place. The first stage involved particle nucleation is considered complete when uninitiated micelles are no longer present and no new particles are formed. This is considered the end of nucleation, end of interval I. About 10-15% of the monomer has normally been converted at this stage (Gordon, 1968 B).

In the interval II, system composed of monomer droplets and polymer particles. The monomer consume by polymerization is replaced by monomer that diffuse from the monomer droplets through the aqueous. Because of the polymerization and monomer transport, the polymer particles grow in size, after some time monomer droplets disappear. This marks the end of interval II. The monomer conversion at which interval II ends depends on the capability of the polymer particle to be swollen by monomer. The higher the maximum swelling, the earlier the monomer droplets disappear. The conversion is typically about 40-60%. During this stage, the particle size increase but the number of particles remains constant (Gordon 1968 B).

In interval III, polymer particles become monomer starved and the concentration of the monomer continuous to decrease toward to end of the polymerization. Thus, polymerization rate will be decrease in interval III. During the third stage, the monomer within the particles is converted to polymer. The rate of reaction decreases as the monomer concentration is decreased (Gordon, 1968 B). The final is water borne, concentrated dispersion tiny polymer particle called latex. The schematic diagram of interval I to interval III was showed in figure 2.2.




I - Initiator * - Initiator molecule ● - surfactant molecule M – monomer
P – polymer chain
Figure 2.2: A schematic diagram of the micelle nucleation model (Chern, 2006).

### 2.2.3 Mechanism of Emulsion Polymerization

Emulsion polymerization involves free radical mechanism which comprise of initiation, propagation and termination. The initiation is achieved in one of two ways, by hemolytic dissociation, using heat or UV light, or by a redox reaction. The well – known initiators used in emulsion polymerization are ammonium persulfate and TBHP. The primary radical must further react with a monomer to begin the polymerization process. This involved the entry of oligomeric radicals into the monomer-swollen micelles or the precipitation of growing radicals from the aqueous phase (Ignac Capek, 2002).

In the case of acrylic resins in emulsion polymerization, the most widely used polymerization technique is free radical polymerization caused by thermal decomposition of a thermally unstable initiator. The sequence for this is as follows:

a) Formation of Radicals and Initiation

The decomposition into free radicals can be represented as:

$$A{-}CO{-}O{-}O{-}CO{-}A \rightarrow A{-}CO{-}O\bullet + A\bullet + CO_2$$

The free radical thus form attack the unsaturated bond of monomer to give a new free radical centre. The polymer chemist selects the type of initiator which best suits the temperature of the polymerization and type of monomers being polymerized.

$$R\bullet \text{ (radical)} + M \text{ (monomer)} \rightarrow RM\bullet$$

b) Propagation

During propagation step, reactive radical will attack another monomer affording long chain polymer particles. The newly formed radical RM• will cause the growth of the polymer chain by successive addition of monomer molecules. The growth of the polymer chain is rapid. The molecular weight of typical acrylic resin is significantly higher than that of typical condensation resins.

The propagation reaction of free radicals with monomer molecules takes place mostly in monomer-swollen particles while monomer droplets only serve as reservoirs to supply the growing particles with the monomer and surfactant species. The particle growth end when the monomer droplets disappear in the polymerization system (Chern, 2006).

$$RM\bullet + M \rightarrow RMM\bullet$$

$$RMM\bullet + M \rightarrow RMMM\bullet$$

$$R(M)_n + M \rightarrow R(M)_{n+1}M\bullet$$

c) Termination

During termination, the growing of polymer particles is terminated by combination or disproportionation. The method of termination, when two growing chains combine is known as termination by combination. The termination reactions can also take place by the reaction of a growing chain with a radical R• produced by decomposition of the initiator. Which reaction path is dominant depends upon the particulars of the monomers and polymerization conditions, with less hindered radicals such as methyl acrylate or acrylonitrile tending to combine, whereas MMA has a greater propensity for disproportionation.

i) Combination

$$R(M)_pM\bullet + R(M)_qM\bullet \rightarrow R(M)_{p+1}R$$

ii) Disproportionation

$$R(M)_pM\bullet + R\bullet \rightarrow R(M)_{p+1}R$$

d) Transfer Reactions

In chain transfer reactions, also known as radical displacement, refers to the premature termination of a growing polymer chain by reaction with another molecule

to create a dead polymer molecule, However, as distinct from the terminations reactions discussed above, which consume radicals, in chain transfer reactions a new radical is generated. The free radical is transferred to another molecule, often by attack on a proton:

$$R(M)_nM\bullet \quad + \quad R'H \quad \rightarrow \quad R(M)_{n+1}H \quad + \quad R'\bullet$$

In many cases, R'H can be solvent, initiator, or another molecule such as chain transfer agent. This process is called intermolecular transfer. The addition of a small quantity of an efficient transfer agent can also be used in order to limit the molecular weight of the polymer.

Nucleation growth of latex particles is very important since it controls the colloidal and physical properties of latex products. Therefore, during the emulsion polymerization, sufficient stirring is very important to confirm the monomer pre-emulsion is equally distributed to whole reaction medium. Absorption is the incorporation of a substance in one state into another of a different state. Desorption is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of absorption. The surfactant molecules adsorbed on monomer droplets may also desorbs out of the droplet surface, diffuse across the continuous aqueous phase and then adsorb on the expanding particle surface. The optimize product quality, residual monomer need to be at minimal. The presence of residual monomer would lead to potential hazard of end-users as well as deteriorating the end product performance.

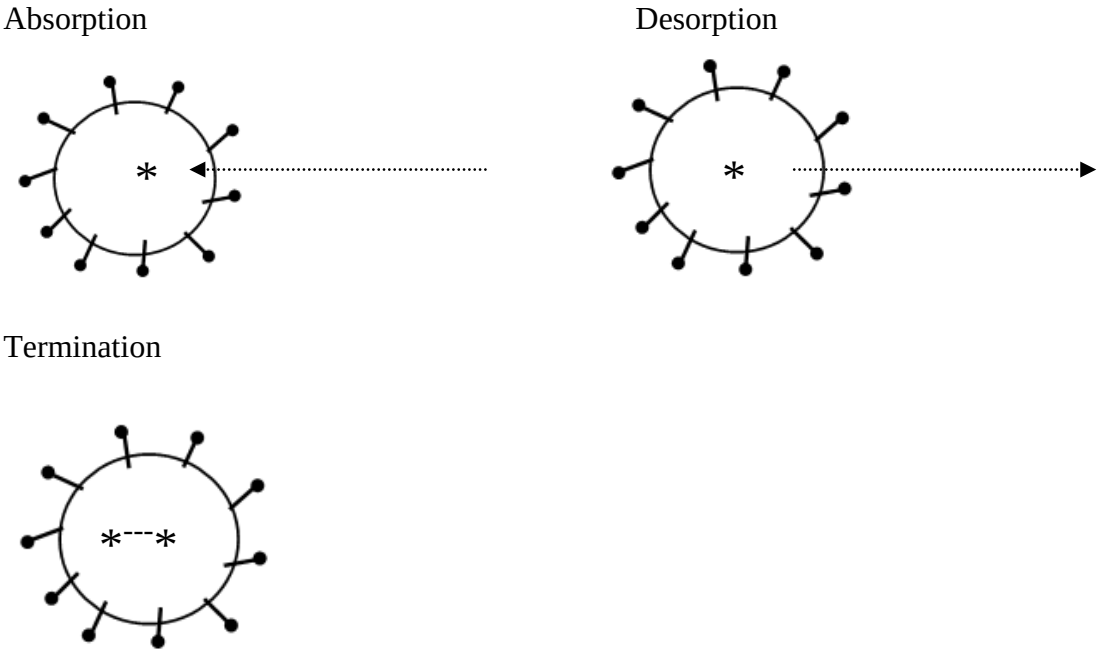



Figure 2.3: A schematic show the mechanism of free radical

### 2.2.4 Semi Batch Emulsion Polymerization

Emulsion polymerizations have been used in batch, semi-batch, and continuous processes. The choice depends on the properties desired in the final polymer or dispersion and on the economics of the product. Batch process refers to where the monomer is first allowed to swell the pre-existing particles and polymerization is conducted subsequently. Semi batch process refers to where the monomer is continuously fed into the reaction medium containing pre-existing particles and polymerized. In continuous process, reactants are continuously fed into the reactor and emerge as continuous stream of product.

It has long been recognized that the reaction pathway in emulsion polymerization plays a decisive role in determining the particle morphology and consequently the emulsion polymers properties. A study of structured polymer latex